Effects of flavour absorption on foods and their packaging materials

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Proefschrift
ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van Wageningen Universiteit, Prof. dr. ir. L. Speelman
in het openbaar te verdedigen
op vrijdag 31 mei 2002
des namiddags te half twee in de Aula.

ISBN: 90-5808-640-2

Abstract

Willige van, R.W.G. (2002). Effects of flavour absorption on foods and their packaging materials. PhD thesis, Wageningen University, The Netherlands, pp 140.

Keywords: flavour absorption, scalping, packaging, food matrix, lldpe, ldpe, pp, pc, pet, pen, β-lactoglobulin, casein, pectin, cmc, lactose, saccharose, oil, modelling, storage, oxygen permeability, taste perception, sensory quality.

Absorption of flavour compounds by linear low-density polyethylene (LLDPE) was studied in model systems representing differences in composition of the food matrix. Proteins, β-lactoglobuline and casein, were able to bind flavours, resulting in suppression of absorption of flavour compounds. Polysaccharides, pectin and carboxymethylcellulose, increased viscosity, and consequently decreased absorption. Disaccharides, lactose and saccharose, increased absorption, probably caused by a 'salting out' effect of less apolar flavour compounds. The presence of a relative small amount of oil (50 g/l) decreased absorption substantially. Combined oily model systems, oil/casein and oil/pectin, showed a similar effect. The extent of absorption of flavour compounds by LLDPE was influenced by food components in the order: oil or fat >> polysaccharides and proteins > disaccharides. A model based on the effect of the polarity (log P) of flavour compounds and on their partitioning coefficients between food(matrix) and packaging material was developed. The model is able to predict absorption of flavour compounds from foods into LLDPE when lipids in the food matrix are the determining factor in flavour absorption. Results show that the model fits nicely with experimental data of real foods skim and whole milk.
LLDPE, polypropylene (PP), polycarbonate (PC), polyethylene terephthalate (PET film and PET bottle) and polyethylene naphthalate (PEN) were immersed in a model flavour solution at different temperatures up to 14 days. The absorption rate and/or total amount of absorbed compounds increased considerably with increasing temperature. Depending on temperature, the total absorption of flavour compounds by the polyolefins (LLDPE and PP) was up to 2400 times higher than by the polyesters (PC, PET and PEN).
The effect of absorbed flavour compounds on the oxygen permeability of low-density polyethylene (LDPE), PP, PC and PET was studied. Due to swelling of the polymers as a result of absorption of flavour compounds, LDPE and PP showed a significant increase of oxygen permeability of 21% and 130%. The oxygen permeability of PC showed a significant decrease of 11% due to occupation or blockage of the 'micro-cavities' by the absorbed flavour compounds. Flavour absorption by PET did not affect the oxygen permeability significantly.
The influence of flavour absorption LDPE, PC and PET on the taste perception of a flavour model solution and orange juice stored in glass bottles was studied with and without pieces of the respective plastic films. Although the content of flavour compounds between controls and polymer treated samples decreased substantially due to absorption, no significant effect on the taste perception of the model solution and orange juice were observed by triangular taste panel tests.

Symbols and abbreviations

β-lg	β-lactoglobulin
η_{sp}	Specific viscosity
ANOVA	Analysis of variance
C*	Coil overlap value (g/l)
CMC	Carboxymethylcellulose
CV	Coefficient of variation
D	Diffusion coefficient, or diffusivity (m^2/s)
E2MB	Ethyl 2-methylbutyrate
EB	Ethyl butyrate
EVOH	Ethylene vinyl alcohol
GC	Gas chromatography
HA	Hexyl acetate
HDPE	High-density polyethylene
K_I	Partition coefficient = m_h/m_l
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
Log P	Measure of hydrophobicity
LVI-GC	Large volume injection gas chromatography
mad	Mean absolute deviation
MDPE	Medium-density polyethylene
OTR	Oxygen transmission rate
P	Permeability coefficient
PC	Polycarbonate
PE	Polyethylene
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
PP	Polypropylene
RSD	Relative standard deviation
S	Solubility coefficient, or solubility (moles/cm^3 atm)
S_x/S_0	Relative absorption (sorption at Xgl^{-1}/ sorption at 0 gl^{-1})
Tg	Glass transition temperature (°C)
VLDPE	Very low-density polyethylene

Aan mijn ouders

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General introduction

1.1 Food packaging

The first and foremost function of a food package is to protect the product and to preserve its inherent quality.[1] An important requirement in selecting packaging systems for foods is the barrier property of the packaging material. To keep a food product crisp and fresh, the package must provide a barrier to moisture. The rancidity of food can be minimized by using packaging material that has a good barrier to oxygen and by protecting a food from light. The original flavour of a food can be maintained by using a packaging material that offers a good barrier to a particular aroma. Thus, properly selected packaging materials are beneficial in extending the shelf-life of foods.[2]

Over the past decades, the use of plastic packaging materials has increasingly replaced metal and glass for food and beverage packaging. The advantages of plastics are numerous: lower costs, lighter in weight, less apt to break or shatter, better for the environment (less energy), transparent, flexible, direct food contact without changing sensory properties, can be reheated in micro-wave (versus metal) and general consumer preference because of convenience. In spite of all these advantages, there are some properties of plastics that limit their use in food and beverage packaging, such as:[3]

1. high gas and water permeability;
2. absorption of food/beverage flavour;
3. low heat resistance (many foods require pasteurisation or sterilisation);
4. not tough enough (brittle);
5. poor appearance;
6. high costs (especially in small packages);
7. migration of low molecular weight compounds (e.g. monomers).

A food's characteristic flavour and aroma are the result of a complex construct of hundreds of individual constituent compounds interacting to produce a recognizable taste and aroma. Thus, if one or more flavour constituents are altered or diminished, food quality may be reduced. A reduction in food quality may result from the oxidation of aroma components due to the ingress of oxygen, or it may be the result of the loss of specific aroma compounds to the packaging material or environment.[4]

1.2 Polymer materials for food packaging

The materials used for the investigations described in this thesis were chosen because of their common use as food packaging materials and their different material characteristics. Material characteristics and applications in food packaging are discussed in the next paragraphs.

1.2.1 Polyolefins

The most widely used polymers for food-packaging applications are the polyolefins, i.e. polyethylene and polypropylene. They are used in direct contact with food since they are chemically inert, thermosealable and provide an excellent moisture barrier. They are used either alone, or as the innermost layer of high barrier packaging structures, like polyethylene laminated aluminium cartons.[5]

1.2.1.1 Polyethylene

Polyethylene (PE) is the most popular plastic in the world. This is the polymer that makes grocery bags, shampoo bottles, film, milk bottles, and children's toys. Polyethylenes are extremely tough, flexible, and chemical resistant. However, their heat resistance, and load bearing capability are limited. For such a versatile material, it has a very simple structure, the simplest of all commercial polymers. PE is a thermoplastic polymer formed from the polymerisation of ethylene (Figure 1.1).

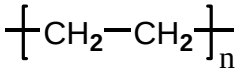

Figure 1.1 Molecular structure of PE.

PE in general is characterised by an extremely regular and flexible molecular chain structure. There are no side groups other than branches of more polyethylene. It is available in a variety of molecular weights and densities, which have been tailored to specific end-use markets.
Density is the most important parameter governing resin properties. PE is essentially a composite material consisting of a rigid crystalline phase and an elastic amorphous phase. As

crystallinity decreases with decreasing density, the product becomes softer and more pliable; clarity and toughness increase. PE can be generally classified on the basis of its density into the product types listed in Table 1.1.[7]

Table 1.1 Commercial classification of polyethylene resins.[7]

Polyethylene product	Density (g/ml)
High-density polyethylene (HDPE)	0.940 – 0.970
Medium-density polyethylene (MDPE)	0.926 – 0.939
Linear low-density polyethylene (LLDPE)	0.915 – 0.926
Very low-density polyethylene (VLDPE)	0.890 – 0.915
Low-density polyethylene (LDPE)	0.915 – 0.940

HDPE has very little side branching (i.e. more densely packed molecular structure), which distinguishes it from LDPE (Figure 1.2). This feature gives it higher thermal resistance and generally better strength properties.

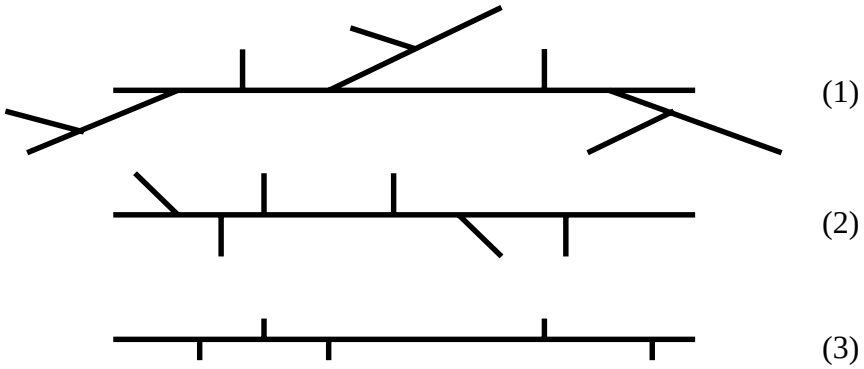

Figure 1.2 Structure of (1) LDPE, (2) LLDPE, and (3) HDPE.[8]

Low-density polyethylene and linear low-density polyethylene

Low-density polyethylene (LDPE) is less ordered than HDPE and has lower crystallinity due to the interference from the side branches. LDPE is made by the high-pressure polymerisation of ethylene (sometimes LDPE is also referred to as high-pressure LDPE or HP-LDPE). About 65% of all the LDPE used in the world today goes into the film and sheet area. These applications include garbage bags, grocery sacks, shrink film, and food packaging.

Linear low-density polyethylene (LLDPE) is very similar to LDPE, except that the branching is much shorter. Density is controlled by the addition of comonomers such as butene, hexene,

or octene. These comonomers give rise to short-chain branches of different lengths, two carbon atoms for butene, four for hexene and six for octene. LLDPE has generally properties in between those of LDPE and HDPE, based on a more limited effect from the side chain branching.[9] LLDPE is much stronger than LDPE, but LDPE is cheaper and easier to produce.[6]

1.2.1.2 Polypropylene

Polypropylene's (PP) chemical structure is very similar to PE, however, on each second carbon atom in the backbone a methyl group is attached (Figure 1.3).

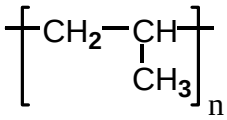

Figure 1.3 Molecular structure of PP.

These methyl groups greatly restrict molecular rotation and flexibility, resulting in significantly greater stiffness than PE. Although much bulkier than PE molecules, PP molecules coil due to the regularity of the methyl groups and flexibility of the backbone. These coils crystallize to a high degree leading to excellent chemical solvent resistance and opacity.

1.2.2 Polyesters

Polyesters have hydrocarbon backbones containing ester linkages, hence the name. The ester groups in the polymer chain are polar, with the carbonyl oxygen atom having a somewhat negative charge and the carbonyl carbon atom having a somewhat positive charge. The positive and negative charges of different ester groups are attached to each other. This allows the ester groups of nearby chains to line up with each other in crystal form.[6] The three most important types of polyesters are polyethylene terephthalate, polyethylene naphthalate and polycarbonate.

1.2.2.1 Polyethylene terephthalate

Polyethylene terephthalate (PET) is produced by a condensation reaction of ethylene glycol and terephthalic acid or dimethyl terephthalate. The molecular structure of PET is given in Figure 1.4.

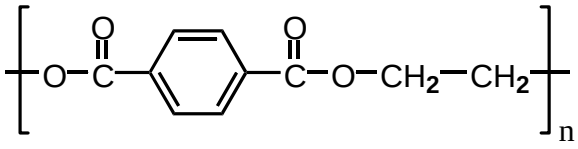

Figure 1.4 Molecular structure of PET.

PET has outstanding properties that make it valuable to the converting and packaging industries. PET film offers mechanical strength, dimensional stability, moisture resistance, chemical resistance, clarity, stiffness, and barrier properties. It is easy to handle well and can be printed or laminated.[10]

1.2.2.2 Polyethylene naphthalate

Polyethylene naphthalate (PEN) is a relatively new family within the polyesters that is getting considerable attention nowadays. In comparison with PET, PEN offers improved performance characteristics, such as better gas barrier properties, higher temperature resistance, higher strength and greater barrier to UV light. The glass transition temperature of PEN is high enough so that it can withstand the heat of both sterilizing bottle washing and hot filling of foods.[6] The raw material essential to PEN production is 2,6 dimethyl naphthalate dicarboxylate (DND). Chemically, the structural differences between PET and PEN is an additional double naphthalate ring in the compound's structure (Figure 1.5).

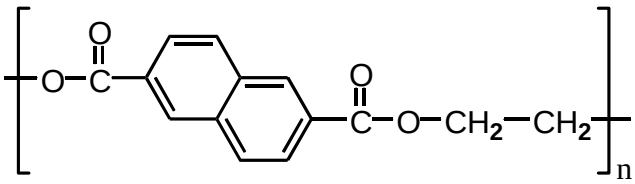

Figure 1.5 Molecular structure of PEN.

PEN copolymers and some high-performance PEN blends may be appropriate for food and beverage packaging, such as beer, baby foods, jams and jellies. However, costs of PEN are approximately six times higher than PET. Therefore, PEN would likely be used for niche markets such as beer, where the superior barrier properties of PEN might cause beer producers to consider PEN over other material choices, despite PEN's higher costs.[10]

1.2.2.3 Polycarbonate

Polycarbonate (PC) is one of the most widely used polymers in electronic product enclosures. Its high strength, toughness, heat resistance, and excellent dimensional and colour stability make it a natural for office product covers and enclosures. PC gets its name from the carbonate group in its backbone chain (Figure 1.6). PC is produced from bisphenol A and phosgene.

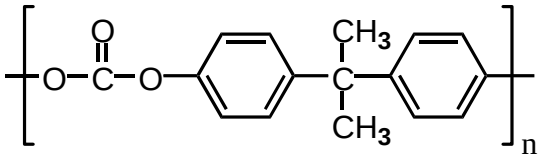

Figure 1.6 Molecular structure of PC.

The phenyl groups present in the main molecular chains and the two methyl side groups, contribute to significant molecular stiffness in polycarbonate. This molecular inflexibility has a major influence on the properties of polycarbonate. The inflexibility and lack of mobility prevents polycarbonate from developing any significant crystal structure. The polymer is therefore classified as amorphous. Due to this amorphous nature, PC has light-transmittance values of 88-91% as compared with 92% for clear plate glass. However, there are a few undesirable properties of polycarbonate. It has only fair chemical resistance, and poor gas and moisture barrier properties. PC is the material of choice for use in reusable bottles, such as water and milk bottles. These bottles take advantage of PC's toughness, clarity and hot-fill capability. The fact that PC is much lighter than glass provides fuel savings as well as productivity improvements, since several bottles can be carried at once.[11]

Table 1.2 shows some of the characteristics of the polymers used in this thesis.

Table 1.2 Characteristics of the polymers used in this thesis.[a]

Polymer	Type / Manufacturer	Polarity	Tg[b] (°C)	Crystallinity (%)	Thickness (μm)	Density (g/cm^3)
LLDPE film	Dowlex 5056E / Dow Benelux	Apolar	-75	45	50	0.921
LDPE film	LDPE 300R / Dow Benelux	Apolar	-75	47	100	0.924
PP film	Bicor® MB200 / Mobil Plastics Europe	Apolar	-5 to 0	80	30	0.916
PC film	Lexan® 8B35 / General Electric Plastics	Polar	+145	0	75	1.20
PET film	Melinex® 800 / DuPont Teijin Films	Polar	+78	45	12, 50 and 75	1.40
PET bottle	- / Schmalbach-Lubeca	Polar	+78	22 to 25	300	1.37
PEN film	Kaladex® 1000 / DuPont Polyester Films	Polar	+120	45	75	1.36

[a] Specifications from manufacturers
[b] Glass transition temperature

1.3 Food-packaging interactions

1.3.1 Permeation, migration and absorption

Interactions within a package system refer to the exchange of mass and energy between the packaged food, the package material and the external environment. Food-packaging interactions can be defined as an interplay between food, packaging, and the environment, which produces an effect on the food, and/or the package.[12]

Mass transfer processes in packaging systems are normally referred to as permeation, migration and absorption (Figure 1.7). Permeation is the process resulting from two basic mechanisms: diffusion of molecules across the package wall, and absorption/desorption from/into the internal/external atmospheres. Migration is the release of compounds from the plastic packaging material into the product.[13] The migration of compounds from polymer packaging materials to foods was the first type of interaction to be investigated due to the concern that human health might be endangered by the leaching of residues from the polymerisation (e.g. monomers, oligomers, solvents), additives (e.g. plasticisers, colourants, UV-stabilisers, antioxidants) and printing inks. Later, absorption, or scalping, of components originally contained in the product by the packaging material attracted attention. Product components may penetrate the structure of the packaging material, causing loss of aroma, or changing barrier and/or mechanical properties, resulting in a reduced perception of quality.[14]

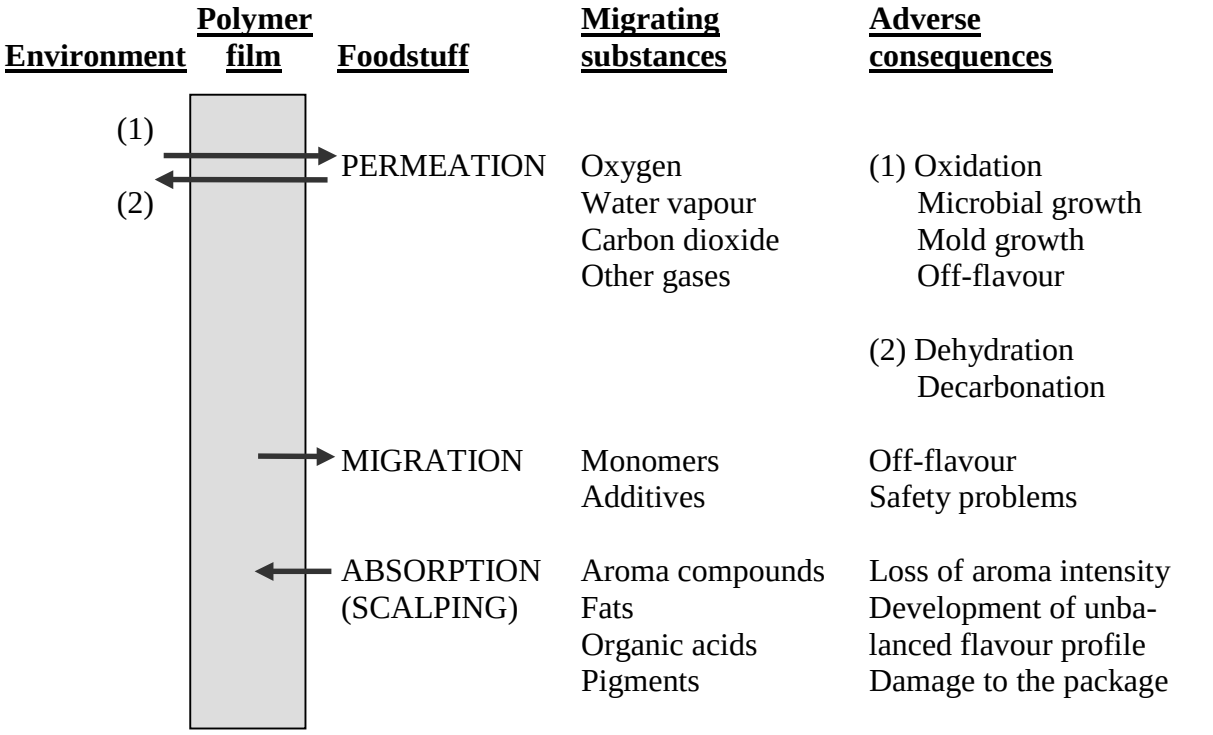

Figure 1.7 Possible interactions between foodstuff, polymer film and the environment, together with the adverse consequences.[1]

1.3.2 Mass transport processes

The fundamental driving force in the transfer of components through a package system is the tendency to equilibrate the chemical potential.[13] Mass transport through polymeric materials can be described as a multistep process (Figure 1.8). First, molecules collide with the polymer surface. Then they adsorb and dissolve into the polymer mass. In the polymer film, the molecules 'hop' or diffuse randomly as their own kinetic energy keeps them moving from vacancy to vacancy as the polymer chains move. The movement of the molecules depends on the availability of vacancies or 'holes' in the polymer film. These 'holes' are formed as large chain segments of the polymer slide over each other due to thermal agitation. The random diffusion yields a net movement from the side of the polymer film that is in contact with a high concentration or partial pressure of permeant to the side that is in contact with a low concentration of permeant. The last step involves desorption and evaporation of the molecules from the surface of the film on the downstream side.[2] Absorption involves the first

two steps of this process, i.e. adsorption and diffusion, whereas permeation involves all three steps.[15]

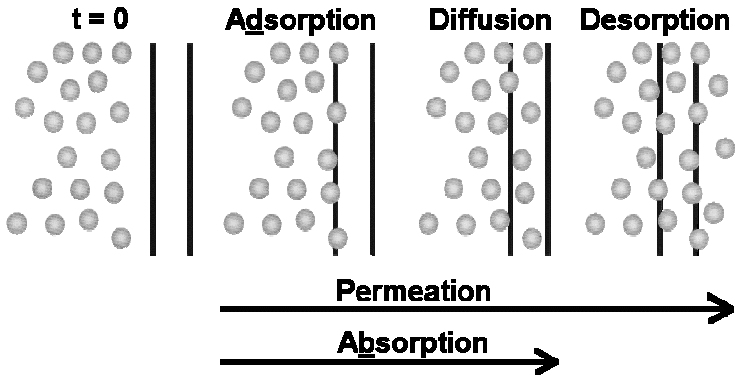

Figure 1.8 Mass transport of molecules through a plastic polymer film.

In virtually every case, the permeation of gases and vapours through non-porous membranes is controlled by the solution and diffusion steps. The diffusion coefficient, *D*, is a measure of the speed of molecules moving in the polymer. The solubility coefficient, *S*, is an indication of the number of permeant molecules that are diffusing. Together, the diffusion coefficient and the solubility coefficient describe the permeability coefficient, *P*.[15]

$$P = D \times S \tag{1}$$

Equation 1 is applicable only for situations where *D* is independent of permeant concentration *c* and *S* follows Henry's law of solubility

$$c = Sp \tag{2}$$

where *p* is the partial pressure of the penetrant.

Mass transport is described by Fick's first law which relates the flux to the driving force

$$Q = -D\frac{\partial C}{\partial x} \tag{3}$$

where *Q* is the flux of permeant per unit area and *x* is the length.

By combining equation 1, 2 and 3, the steady state rate of permeation through a polymer film with a cross-sectional area *A* and thickness *L* is given by equation 4,

$$\frac{\Delta M_x}{\Delta t} = \frac{PA\Delta p_x}{L} \tag{4}$$

where M is the quantity of permeant *x*, *t* is time, and Δp_x is the difference in partial pressure of the permeant on the two sides of the film.[15]

Although there are similarities between gaseous and liquid transport in a polymer, there are also a number of differences. In general, the affinity between liquids and polymers is much greater than that between gases and polymers, i.e. the solubility of a liquid in a polymer is much higher than that of a gas. Another difference between liquids and gases is that gases in a mixture permeate through a polymer in quite an independent manner, whereas with liquid mixtures the transport of the components is influenced by thermodynamic interaction (such as solubility and polarity).[16] When the permeation process involves highly interactive organic penetrants such as aroma, flavour, or solvent molecules, the diffusion process is more complex than the diffusion of simple gases, and the diffusion coefficient may vary as a function of penetrant concentration and time. Fick's second law (equation 5), which is derived from Fick's first law, describes the non-steady state where the concentration gradient is a function of distance *x* and time *t*, if the diffusion coefficient is assumed to be constant.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{5}$$

When *D* varies with *t*, the diffusion is often called *non-Fickian*.[17]

1.4 Flavour absorption

As polymer packaging is more and more widely used for direct contact with foods, product compatibility with the packaging material must be considered. The absorption of flavour compounds, or scalping, is one of the most important compatibility problems. Aroma absorption by plastic packages has been recognized for many years.[14] Several research groups

throughout the world investigated flavour absorption phenomena extensively. It is a complex field, and several factors have been proven to have important effects on the extent of absorption of different flavour compounds by various packaging materials.[1]

1.4.1 Factors affecting flavour absorption

An understanding of absorption between flavour compounds and polymeric packaging materials requires knowledge of the chemical and physical structures of both the flavour compound and the polymer.

1.4.1.1 Polymer properties

The properties of a plastic packaging material are the foremost important parameters that control the amount of flavour absorption. The properties of a polymer result from its chemical nature, morphology, formulation (compounding with additives), processing, and even storage and conditions of use. Important parameters derived from the chemical structure, such as glass transition temperature, crystallinity and free volume that have an effect on flavour absorption are essentially determined upon the selection of a particular polymer.

Glass transition temperature (Tg)

Figure 1.9 shows the behaviour of one of the many properties of an amorphous and semicrystalline polymer: the modulus of elasticity.

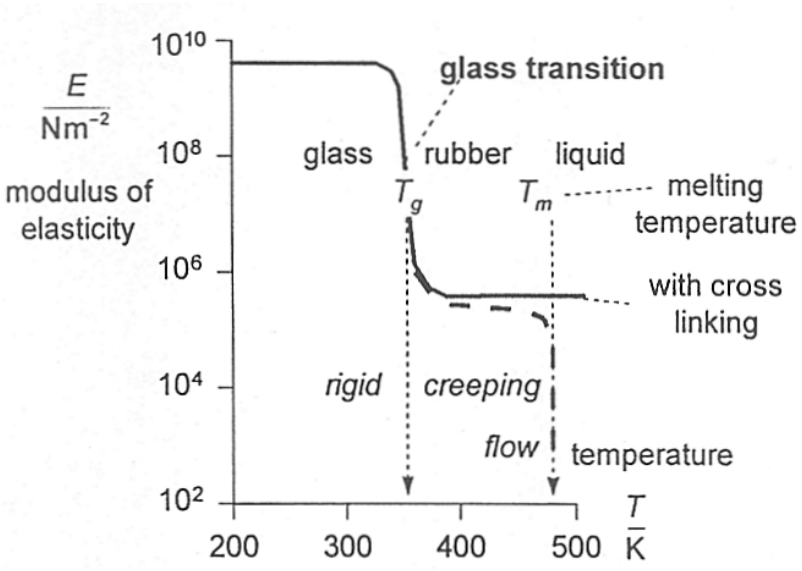

Figure 1.9 Modulus of elasticity against temperature, showing the glass transition and melting temperatures.[18]

There are two sharp breaks indicating phase transitions. At low temperatures the polymer is rigid and brittle: it forms a *'glass'*. At the glass transition temperature Tg the modulus of elasticity drops dramatically. Many of the properties of the polymer change a little at this temperature. Above Tg the polymer becomes soft and elastic; it forms a *'rubber'*. At high temperatures, the polymer may melt, to form a viscous liquid.[18] The polymers that we know as glassy polymers, such as the polyesters PET, PC and PEN, have a Tg above ambient temperature. At room temperature, glassy polymers will have very stiff chains and very low diffusion coefficients for flavour molecules at low concentrations. Rubbery polymers such as the polyolefins PE and PP have a Tg below ambient temperature. Rubbery polymers have high diffusion coefficients for flavour compounds and steady-state permeation is established quickly in such structures.[17] Stiff-chained polymers that have a high glass transition temperature generally have low permeability, unless they also have a high free volume.[4]

Free volume

The free volume of a polymer is the molecular 'void' volume that is trapped in the solid state. The permeating molecule finds an easy path in these voids. Generally, a polymer with poor symmetry in the structure, or bulky side chains, will have a high free volume and a high permeability.[3]

Crystallinity

The importance of crystallinity to absorption has been recognized for many years. All polymers are at least partly amorphous; in the amorphous regions the polymer chains show little ordering. However, polymers often contain substantial 'crystalline' parts, where the polymer chains are more or less aligned (Figure 1.10).

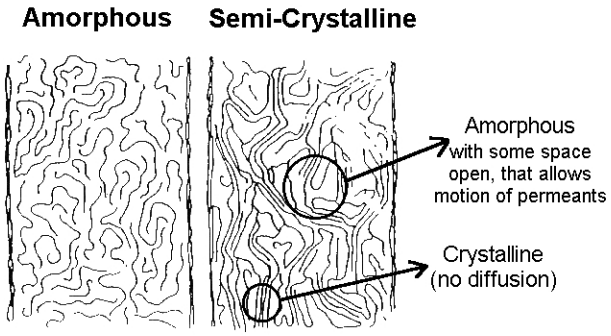

Figure 1.10 An amorphous polymer (left) and a semi-crystalline polymer (right) with amorphous regions (permeable) and crystalline regions (impermeable).

The crystalline areas are a tenth denser than the amorphous parts; for many permeants they are practically impermeable. So, diffusion occurs mainly in the amorphous regions in a polymer, where small vibrational movements occur along the polymer chains. These micro Brownian motions can result in 'hole' formation as parts of the polymer chains move away from each other. It is through such 'holes' that permeant molecules can diffuse through a polymer.[14,18] Therefore, the higher the degree of crystallinity in a polymer, the lower the absorption.

1.4.1.2 Flavour properties

Concentration

There are relatively few reports relating flavour absorption to the relative concentrations of the sorbants in a liquid or vapour. Mohney *et al*.[19] reported that low sorbant concentrations will only affect the polymer to a very limited extent and the amount of absorbed compounds will be directly proportional to the concentration of the sorbants. At higher concentrations, however, the absorption of compounds into a polymer material may alter the polymer matrix by swelling.[20,21] Consequently, to avoid overestimation of the amounts of absorbed

compounds or swelling of the polymer, it is advisable to use a mixture of compounds in the concentration range that can be expected to be found in a food application.[22] However, to generate reliable and reproducable analytical data, experimental procedures are usually carried out with enhanced concentrations.

Presence of a copermeant

Interactions between different flavour compounds may also affect the absorption of low molecular weight compounds into polymer food packaging materials.[23-25] Some flavour compounds exhibit a lower absorption rate in mixtures compared to systems containing the individual flavour compounds. This may be due to a competition for free sites in the polymer and/or alteration of the partitioning between the solution and the polymer due to an altered solubility of the compounds in the solution. Therefore, the use of single compound model solutions may cause an overestimation of the amount absorbed in an actual food packaging application.[22]

Polarity

The polarities of a flavour compound and polymer film are an important factor in the absorption process. The absorption behaviour of different classes of flavour compounds depends to a great extent on their polarity. Different plastic materials have different polarities; hence their affinities toward flavour compounds may differ from each other.[26] Flavour compounds are absorbed more easily in a polymeric film if their polarities are similar.[27] Polyolefins are highly lipophilic and may be inconvenient for packaging products with non-polar substances such as fats, oils, aromas etc., since they can be absorbed and retained by the package.[5] The polyesters, however, are more polar than the polyolefins and will therefore show less affinity for non-polar substances.

Molecular size and structure

The size of the penetrant molecule is another factor. Smaller molecules are absorbed more rapidly and in higher quantities than larger molecules. Very large molecules plasticize the polymer, causing increased absorption into the newly available absorption sites.[28] Generally, the absorption of a series of compounds with the same functional group increases with an increasing number of carbon atoms in the molecular chain, up to a certain limit. Shimoda *et al.*[29] reported that absorption of aldehydes, alcohols and methyl esters increased with increasing molecular weight up to about 10 carbon atoms. For even larger molecules the

effect of molecular size overcomes the effect of the increased solubility of the compounds in the polymer, and the solubility coefficient decreases. Linssen *et al.*[30] reported that compounds with eight or more carbon atoms were absorbed from yoghurt drinks by HDPE, while shorter molecules remained in the product. They also observed that highly branched molecules were absorbed to a greater extent than linear molecules.

1.4.1.3 External properties

Food matrix

The composition of a food matrix plays a major role in the absorption of flavour compounds. Flavours may be dissolved, adsorbed, bound, entrapped, encapsulated or diffusion limited by food components. Proteins, carbohydrates and oil interact with flavours, changing the concentration of free flavour in the solution and consequently increasing or decreasing the amount of absorption. Van Willige *et al.*[31] described that the extent of flavour absorption by LLDPE is influenced by food components in the order: oil or fat >> polysaccharides and proteins > disaccharides. Because of the lipophilic character of many flavour compounds, food products with a high oil/fat content will lose less flavour by absorption into LLDPE packaging than food products containing no or a small quantity of oil.[32]

Temperature

Temperature is probably the most important environmental variable affecting transport processes. The permeability of gases and liquids in polymers increases with increasing temperature according to the Arrhenius relationship. Possible reasons for increased flavour absorption at higher temperatures are:[26]

- increased mobility of the flavour molecules;
- change in polymer configuration, such as swelling or decrease of crystallinity;
- change in the volatile solubility in the aqueous phase.

Relative humidity

For some polymers, exposure to moisture has a strong influence on their barrier properties. The presence of water vapour often accelerates the diffusion of gases and vapours in polymers with an affinity for water. The water diffuses into the film and acts like a

plasticiser. Generally, the plasticising effect of water on a hydrophilic film, such as ethylene-vinyl alcohol (EVOH) and most polyamides, would increase the permeability by increasing the diffusivity because of the higher mobility acquired by the polymer network.[14] Absorbed water does not affect the permeabilities of polyolefins and a few polymers, such as PET and amorphous nylon, show a slight decrease in the oxygen permeability with increasing humidity. Since humidity is inescapable in many packaging situations, this effect cannot be overlooked. The relative humidity in the environment is often above 50%, and the relative humidity inside a food package can be nearly 100%.[15]

1.4.2 Effects of flavour absorption

Flavour absorption may affect the flavour of a product as well as the mechanical properties of the polymer, such as tensile and heat seal strength and permeability, or cause delamination of the polymeric structure.[33] Two effects of flavour absorption were investigated in this thesis, the effect of flavour absorption on oxygen permeability of a polymer and on the taste perception of a product.

1.4.2.1 Effect on oxygen permeability of a plastic package

The shelf-life of a food or beverage packaged in a polymer will depend on many factors, but one of the most important is the rate at which oxygen from the air enters the package. For some foods, the oxygen tolerance is high, such as salad dressings, peanut butter, most soft drinks and high alcohol liquor. For other foods, the oxygen tolerance is very low, such as beer, low-acid foods, wine, coffee, or baby foods.[3] Little information is available in literature about the influence of absorbed flavour compounds on the oxygen permeability of packaging materials. Hirose *et al.*[33] reported that the oxygen permeability of LDPE and two types of ionomer increased due to the presence of absorbed d-limonene. Sadler and Braddock[21] showed that the oxygen permeability of LDPE was proportional to the mass of absorbed limonene. In another paper, they concluded that oxygen permeability of LDPE and the diffusion coefficients of citrus flavour volatiles in LDPE were related to the solubility of these compounds in the polymer.[34] An increased oxygen permeability of LDPE indicated that absorption of volatiles must be responsible for structural changes in the polymer.

1.4.2.2 Effect on sensory properties of a food product

Absorption of aroma compounds by plastics can affect the sensory quality of foods. The effect may be an overall loss of odour intensity or a change in the aroma character. A change in character can occur when only certain components of a complex aroma mixture are absorbed.[28] However, investigations about the relevance of the loss of flavour compounds for the sensory quality of a product are insufficient and sometimes contradictory because flavour alteration depends on many parameters, such as storage temperature and type of packaging material.[26] Knowledge of the impact that the loss of aroma compounds by absorption into polymer packages has on the sensory quality of foods is important to food and beverage manufacturers. Appropiate use of polymers with a very low absorption to important aroma/flavour compounds will diminish losses to levels below human sensory detection.[28]

1.5 Aim and outline of this thesis

In this thesis different aspects of flavour absorption by packaging materials have been studied: the influence of the food matrix and storage conditions on the extent of flavour absorption, and the influence of flavour absorption on the oxygen permeability of the polymer and the sensory quality of a product. It is well documented that flavour compounds are absorbed by plastic packaging materials. However, in reviewing the literature, investigations about the influence of the food matrix on flavour absorption and how flavour absorption affects the oxygen permeability of a package and sensory profile of a product are insufficient. In **chapter 2 and 3**, the effects are described of differences in food matrices on the absorption of flavour compounds by LLDPE using a large volume injection GC 'in vial' extraction method. The investigated food components and real food products included β-lactoglobulin (β-lg), casein, pectin, carboxymethylcellulose (CMC), lactose, saccharose, oil/water emulsions, oil/casein models, oil/pectin models, skim milk and whole milk. In **chapter 4**, a model is proposed which can predict flavour absorption from oil containing food products by LLDPE using the data from chapter 2 and 3. In **chapter 5**, the influence of storage time and temperature on absorption of flavour compounds from solutions by plastic packaging materials is described. **Chapter 6** reports on the influence of flavour absorption on oxygen permeation through LDPE, PP, PC and PET plastics food packaging materials.

Chapter 7 deals with the influence of flavour absorption by LDPE, PC and PET food packaging materials on taste perception of a model solution and orange juice. Finally, the concluding remarks and summary in **chapter 8** give an overview of the studies described in this thesis.

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2

Influence of food matrix on absorption of flavour compounds by linear low-density polyethylene: proteins and carbohydrates

Abstract

The effects of differences in food matrices on the absorption of four flavour compounds (limonene, decanal, linalool and ethyl 2-methylbutyrate) into linear low-density polyethylene (LLDPE) were studied by using a Large Volume Injection GC 'in vial' extraction method. Food components investigated included β-lactoglobulin (β-lg), casein, pectin, carboxymethylcellulose (CMC), lactose and saccharose. β-lg interacted irreversibly with decanal ($P<0.01$) and suppressed absorption of the latter by LLDPE by more than 50% after 14 days of exposure. Casein was capable of binding limonene and decanal ($P<0.05$) by hydrophobic and covalent interactions, resulting in decreased absorption of 40% and 90%, respectively. The absorption rates of limonene and to a leaser extent of decanal were decreased in presence of pectin and CMC. Increasing viscosity slowed down diffusion of flavour compounds from the matrix to LLDPE. An increase of absorption ($P<0.01$) was observed for linalool and ethyl 2-methylbutyrate, due to a 'salting out' effect caused by lactose and saccharose. The absorption of decanal was decreased ($P<0.01$) after 14 days of exposure in the presence of lactose, saccharose and CMC. There might be an interactive effect between a sugar(residu) and decanal. Knowledge of the composition of a food matrix and packaging material showed to be necessary to estimate the amount of flavour absorption.

This chapter has been published as:

Van Willige RWG, Linssen JPH and Voragen AGJ, *J Sci Food Agric* **80:**1779-1789 (2000).

2.1 Introduction

Synthetic polymers are more and more used as packaging materials for food. The quality and the shelf life of the packaged food depend strongly on physical and chemical properties of the polymeric film and the interactions between food components and package during storage. Food-packaging interactions can be defined as an interplay between food, packaging, and the environment, which produces an effect on the food, and/or package.[1] One of these interactions is flavour absorption (or scalping), meaning that aroma compounds from the food are able to migrate into the package. Several investigations have shown that considerable amounts of aroma compounds can be absorbed by plastic packaging materials, which can cause loss of aroma intensity or an unbalanced flavour profile.[2-6] Absorption may also indirectly affect the food quality by causing delamination of multilayer packages[7,8] or by increasing oxygen transmission through the packaging material.[9,10]

Several factors influence the amount of absorption of flavour compounds into polymeric packaging materials. The chemical composition, morphology and crystallinity of the polymer, as well as the chemical composition, concentration and mixture of the sorbants are important criteria. External factors like storage time, relative humidity, temperature and pH can also affect solubility of aroma compounds in a polymer.[5,11-13] Little information is available in literature about the influence of the food matrix on flavour absorption by polymers. Linssen *et al.*[14] and Yamada *et al.*[15] showed that the presence of juice pulp in orange juice decreased absorption of volatile compounds into polymeric packaging materials. They suggested that pulp particles are holding flavour compounds (eg limonene) in equilibrium with the watery phase, which could be responsible for the decrease of absorption of these compounds by the plastics.

Fukamachi *et al.*[16] studied the absorption behaviour of flavour compounds from an ethanolic solution as a model of alcoholic beverages. The absorption of a mixture of homologous volatile compounds (esters, aldehydes and alcohols with carbon chain length 4-12) into LDPE film first increased with a maximal absorption at 5-10% (v/v) aqueous ethanol and then decreased remarkably with increasing ethanol concentration. Ethylene Vinyl Alcohol (EVOH) film showed similar absorption behaviour, with maximal absorption at 10-20% (v/v) aqueous ethanol. Nielsen *et al.*[5] investigated the effects of olive oil on flavour absorption into LDPE. Olive oil and, thereby, the flavours dissolved in the oil, were absorbed in large amounts by the plastic. The partition coefficients for alcohols and short-chained esters in an

oil/polymer system were higher than in a water/polymer system, while the partition coefficients for aldehydes and long-chained esters were lower in an oil/polymer system than in a water/polymer system. Not only the type of plastic used is of importance for the uptake of aroma compounds, but also possible interactions between flavour and food components. Flavour components may be dissolved, adsorbed, bound, entrapped, encapsulated or retarded in their diffusion through the matrix by food components. The relative importance of each of these mechanisms varies with the properties of the flavour chemical (functional groups, molecular size, shape, volatility, etc.) and the physical and chemical properties of the components in the food.[17,18]

Knowledge of the binding behaviour of flavour components to non-volatile food components and their partitioning between different phases (food component/water and water/polymer) is of great importance in estimating the rate and amount of absorption by polymers. Our objective was to investigate the influences of the food matrix on the absorption of flavour compounds. In this paper the effects of non-fatty food constituents, proteins and carbohydrates, on the absorption of different flavour compounds by linear low-density polyethylene are studied.

2.2 Materials and methods

2.2.1 Materials

Linear low-density polyethylene (LLDPE) film, thickness 50 μm and density 925 kg/m^3, was manufactured at Dow Benelux N.V. (Terneuzen, The Netherlands).

Ethyl 2-methylbutyrate (E2MB) and linalool were purchased from Acros, decanal from Merck and (+)-limonene from Sigma. The aroma compounds were selected based on differences in functional groups and polarity, see Table 2.1. Log P represents the hydrophobicity of a flavour compound; the higher the log P, the more hydrophobic a compound.

Table 2.1 Characteristics of the flavour compounds used in the model solutions.

Flavour compound	bp (°C)	Log P[a]	Solubility[b] (g/l)	Density (g/ml)	Purity (%)
Limonene	178	4.58	0.0027	0.84	99
Decanal	208	4.09	0.012	0.83	97
Linalool	195	3.28	0.11	0.87	99
E2MB	133	2.12	2.47	0.87	99

[a] Measure of hydrophobicity, calculated with ACD/Log P v3.6 using the ACD/I-Lab service[32]
[b] Solubility at 25ºC in water, calculated with ACD/Aqueous Solubility v4.0 using the ACD/I-Lab service[32]

Tween 80 from Merck was used as an emulsifier, to stabilize the flavour compounds in an aqueous phase. The non-volatile components used were: β-lactoglobulin (>90%) from Besnier-Bridel (Massy, France), casein (bovine milk, 88% protein) from Sigma, pectin (GENU beta pectin; DE 57% and DA 23%) from Hercules (Barneveld, The Netherlands), low substituted carboxymethylcellulose (CMC) (AKU LZ 855; SD=0.85) from Akzo (Arnhem, The Netherlands) and lactose (monohydrate) and saccharose from Merck.

2.2.2 Preparation of model flavour solutions

A flavour stock solution was prepared in a stoppered conical flask by dissolving the four aroma compounds in 8 g/l aqueous Tween 80 each in a concentration of 200 µl/l. Flavour compounds were added using a micropipet (Micropipette) equipped with a glass capillary tube (Socorex, Lausanne, Switzerland). The Micropipette always dispenses the same volume regardless of viscosity. The solution was vigorously stirred at room temperature using a magnetic stirrer. Preliminary investigations had shown that the solution was homogeneous after 4h of stirring.

Non-volatile component stock solutions were prepared in stoppered conical flasks at six different concentrations: β-lactoglobulin and casein at 0, 10, 20, 40, 60 and 80 g/l; pectin and CMC at 0, 10, 20, 30, 40 and 50 g/l; lactose and saccharose at 0, 10, 20, 50, 100 and 200 g/l.

The final model solutions were prepared by adding 100 ml of the flavour stock solution to 100 ml of the non-volatile stock solutions giving a final flavour concentration of 83 mg/l of decanal, 84 mg/l of limonene, 87 mg/l of E2MB and 87 mg/l of linalool in 4 g/l of aqueous Tween 80. The final non-volatile component concentrations were 0, 5, 10, 20, 30 and 40 g/l for β-lactoglobulin and casein, 0, 5, 10, 15, 20 and 25 g/l for pectin and CMC and 0, 5, 10,

25, 50 and 100 g/l for lactose and saccharose. The model solutions were then equilibrated overnight at 4°C using a magnetic stirrer.

2.2.3 Exposure conditions

Strips of LLDPE (1.5 x 2.0 cm, 13.9 ± 0.1 mg) were individually placed into 15-ml Teflon screw cap vials (Supelco), and fully immersed in the model solution (15 ml). Samples were stored in the dark at 4°C. No significant changes in pH and colour were observed in the model solutions during storage. After 1, 5 and 14 days of contact, strips and model solutions were analyzed in duplicate using Large Volume Injection GC (LVI-GC) and static headspace GC, respectively.

2.2.4 LVI-GC 'in-vial' extraction of the LLDPE strips

The LLDPE strip were removed from the vials, thoroughly wiped with paper tissue to remove excess model solution, and immediately placed into a 10-ml vial containing 5 ml n-hexane (Enviroscan, Lab-scan, Dublin, Ireland). The vials were tightly closed with a Teflon/silicone seal and an aluminium crimp cap. In-vial extraction was carried out for 30 minutes in an ultrasonic bath (Ultrawave, Cardiff, UK). Longer ultrasonic treatment did not achieve better

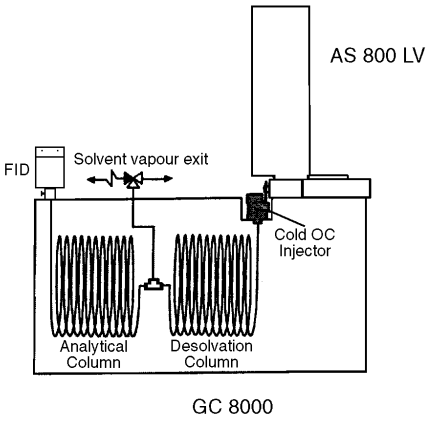

Figure 2.1 LVI-GC system for large volume on-column injection.

extraction. GC analysis was performed using a LVI-GC system (Ultra Trace^{TM}) (Interscience, Breda, The Netherlands). Ultra-Trace GC (see Figure 2.1) is based on the highly selective

separation of the analytes from the large amount of solvent by partial evaporation of the solvent into a desolvation precolumn through an automated valve. The technique not only eliminates tedious and time consuming reconcentration steps, but also provides more accurate results (no loss of resolution and sample integrity). The system consisted of an AS 800 autosampler, a Carlo Erba GC 8000 Top series (Interscience, Breda, The Netherlands) equipped with a Digital Pressure Flow Control (DPFC), an on-column injector, a 15 m x 0.53 mm i.d. UNCORET^{TM} desolvation column (MEGA, Italy), a 30 m x 0.32 mm i.d. df=0.25 μm DB-1701 (J&W Scientific) analytical column, a heated solvent vapour exit (SVE) and a FID-detector. The LVI-GC conditions used are listed in Table 2.2. Data were recorded and handled with Chrom-Card software (CE instruments, Milan, Italy). Calibration curves (r^2>0.997) were established for each component with the external standard method.

Table 2.2 Large Volume Injection GC conditions.

Conditions	Value
Carrier gas	Helium (constant flow 2.3 ml/min)
Injection volume	30 μl hexane extract
Injection speed	5 μL/s
Secondary cooling time	11 s
SVE delay time	11 s
SVE temperature	200°C
FID detector temperature	290°C
Oven programme	50°C (10') => 5°C/min => 150°C => 25°C/min => 280°C (5')

2.2.5 Static Headspace GC extraction of the model solutions

One hundred microlitres of the model solution was pipetted (using a Micropipette) in a headspace vial and closed with a Teflon/butyl seal and magnetic crimp cap. Static headspace GC was carried out using a Fisons Instruments, headspace autosampler HS 800 (Interscience). A Carlo Erba Instruments HRGC 5300 Mega series gas chromatograph equipped with a MFA 815 cold trap Fisons Instruments and FID detector was used (Interscience, Breda, The Netherlands). The column was a 30 m x 0.53 mm id df=1.0 μm, fused silica DB-Wax column (J&W Scientific). Data were recorded and handled with Chrom-Card software. Calibration curves (r^2>0.996) were established for each component by direct

injection of each component dissolved in hexane. The headspace sampler, cold trap and GC conditions used are given in Table 2.3.

Table 2.3 Static headspace sampler, cold trap and GC conditions.

Conditions	Value
Automated headspace sampler	
Temperature sampling tray	4°C
Equilibrium time	20 min
Equilibrium temperature*	30°C
Stirring speed (10s on; 10s off)	2000 rpm
Temperature of injection syringe	70°C
Volume of headspace injected	500 µl
Cold Trap conditions	
Cooling temperature	-75°C
Time	20 s
Desorption temperature	240°C
GC conditions	
Carrier gas	Helium (30 kPa)
Injector temperature	200°C
FID detector temperature	250°C
Oven programme	80°C => 5°C/min => 110°C => 10°C/min => 200°C

* An incubation temperature of 30°C was chosen to prevent denaturation of proteins.

Because the initial mass (m_0) of the flavour compounds in the solution is known, the partition coefficient (K_I) of flavour compound I is calculated from a triplicate determination at t=0 with:

$$K_I = m_H/m_L = m_H/(m_0 - m_H); \qquad m_H = V_H/V_{Inj} \times m_{Inj}$$

m_H = mass of the flavour compound in the headspace at equilibrium, m_L = mass of the flavour compound in the liquid phase at equilibrium, m_0 = initial mass of the flavour compound in the solution at t=0 ($m_0 = m_H + m_L$), m_{Inj} = mass of the flavour compound injected (determined with calibration curve), V_{Inj} = volume of the headspace injected (= 0.5 ml), V_H = volume of the headspace (= 12.22 ml ± 0.076). Assuming that the partition coefficient K_I is constant

during the experiment, the mass of each aroma component in the model solution (100 µl) after t=1, 5 and 14 days can be calculated with:

$$m_{t,I} = m_H/K_I + m_H$$

2.2.6 Viscosity measurements

The viscosity's (η) of pectin and CMC model solutions were measured to study the influence of viscosity on the rate of absorption. A Bohlin VOR Rheometer (Bohlin Reologi, Lund, Sweden) with a concentric C25 cylinder at shear rates ranging from 1.46 to 58.1 s^{-1} at 4°C was used. When viscosity was plotted versus shear rate, all concentrations showed Newtonian flow (horizontal line).

2.2.7 Statistical analysis

All determinations were carried out in duplicate. Data were subjected to one-way analysis of variance (ANOVA) with concentrations of a food component as the main effect. Differences between concentrations of a food component were tested by comparing mean values with the Duncan test when ANOVA was significant ($P<0.05$).

2.3 Results and discussion

2.3.1 Absorption of flavour compounds by LLDPE

Table 2.4 and 2.5 set out the absorption values (mg/g LLDPE) and remaining concentrations in model solutions of limonene, decanal, linalool and E2MB by LLDPE after 1, 5 and 14 days of exposure at 4°C. The possible (additional) amount of flavour compounds absorbed by the cut-edges of the strips (edge absorption) was assumed constant for all samples. When a food component had a statistical significant effect on the absorption of a flavour compound

Table 2.4 Concentration[a] of limonene and decanal in LLDPE and model solution at different concentrations of food components after 1, 5 and 14 days at 4°C.

		Limonene						Decanal					
Food	Conc.	LLDPE (mg/g)			Model solution (mg/l)			LLDPE (mg/g)			Model solution (mg/l)		
component	(g/l)	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14
ß-lg	0	11.78	13.69a	15.15ab	67.28	63.09	57.84	3.68a	3.53a	3.22a	78.69	80.07	57.92
	5	11.02	13.73a	15.27ab	68.13	62.79	59.08	3.20ab	3.05b	0.96b	82.13	78.37	25.42
	10	11.91	15.60b	16.67a	67.68	57.54	57.93	3.14ab	3.17b	1.50c	81.91	76.55	34.15
	20	11.28	14.62ab	14.24bc	67.93	63.69	58.18	2.61bc	2.51c	1.94d	81.47	86.26	57.06
	30	10.68	15.79b	14.43bc	68.45	63.18	58.79	2.09cd	2.35c	1.87d	84.47	89.64	59.23
	40	11.32	15.49b	13.04c	67.77	62.48	59.10	1.90d	1.88d	1.41c	84.77	85.54	60.49
Average mad (%)[b]		5.61	2.07	2.89	0.15	0.92	0.56	3.75	1.97	4.42	1.15	0.49	4.26
ANOVA[c]		NS	P<0.05	P<0.05				P<0.01	P<0.01	P<0.01			
Casein	0	13.00a	16.32a	16.04a	68.37	61.65	57.30	4.10a	4.01a	3.93a	81.14	82.18	59.94
	5	12.08b	16.09a	15.58a	70.23	62.09	59.37	4.02a	3.09b	0.14b	84.09	13.15	3.07
	10	11.53b	16.00a	15.26a	80.55	71.57	66.33	3.82a	2.44b	0.64c	89.32	16.92	3.31
	20	8.78c	13.60b	13.85b	81.27	70.63	67.37	3.24ab	2.94b	0.45bc	91.06	4.52	0.95
	30	8.35cd	12.84bc	13.53b	82.70	73.46	69.47	3.04ab	1.47c	1.09d	87.25	4.87	3.73
	40	7.62d	12.30c	13.32b	78.00	69.64	65.61	2.02b	2.16bc	1.39d	81.27	3.82	1.20
Average mad (%)		2.10	1.55	1.50	0.50	0.28	0.68	7.34	9.66	12.91	0.97	13.30	21.37
ANOVA		P<0.01	P<0.01	P<0.01				P<0.05	P<0.01	P<0.01			
Pectin	0	12.14a	15.56a	15.47a	68.36	63.31	61.66	4.17a	4.19a	3.02a	82.26	78.33	66.57
	5	10.74a	15.61a	16.03a	70.48	63.23	60.90	4.15a	4.00ab	2.87a	81.48	79.61	70.92
	10	8.86b	13.92b	15.47a	74.85	66.45	61.45	3.84ab	3.88b	2.44b	85.43	83.40	75.87
	15	6.73c	11.23c	12.93b	76.19	68.59	61.75	3.43cd	3.63c	3.09a	82.51	80.33	72.92
	20	6.43c	11.04c	12.42b	76.24	66.69	60.82	3.54bc	3.62c	3.10a	83.09	79.14	74.86
	25	5.18c	10.12d	12.34b	76.39	67.38	59.89	3.09d	3.53c	3.21a	82.13	77.68	76.20
Average mad (%)		4.21	0.98	1.99	0.84	0.98	1.48	2.02	1.31	2.73	0.92	1.59	1.56
ANOVA		P<0.01	P<0.01	P<0.01				P<0.01	P<0.01	P<0.05			
CMC	0	10.62a	15.37a	16.04ab	65.19	57.59	63.08	4.08ab	4.19ab	3.21a	80.71	75.27	71.96
	5	10.54a	14.97a	17.24a	68.27	57.98	62.95	4.42a	4.22a	1.80b	80.53	72.88	51.19
	10	8.80b	13.47b	16.57a	71.48	61.82	63.33	4.08ab	4.11ab	1.29c	80.23	73.48	43.26
	15	7.44c	11.55c	14.63bc	72.38	68.53	64.06	3.99abc	3.94ab	1.28cd	83.03	82.08	54.49
	20	6.38cd	10.10d	13.21c	71.29	68.65	65.09	3.80bc	3.79bc	1.06cd	76.21	75.97	51.27
	25	5.68d	9.24d	11.28d	73.12	71.20	60.39	3.57c	3.51c	0.88d	76.07	76.97	53.64
Average mad (%)		2.69	1.70	2.90	0.81	1.49	4.38	2.80	2.15	5.91	0.97	1.48	5.98
ANOVA		P<0.01	P<0.01	P<0.01				P<0.05	P<0.05	P<0.01			
Lactose	0	13.33a	15.59	15.40	63.33	60.46	53.81	4.58	3.90	3.76a	84.01	82.32	69.71
	5	13.08a	15.79	15.30	65.83	61.80	55.58	4.67	4.03	3.20b	82.55	83.09	62.87
	10	12.83a	16.53	15.94	66.63	61.50	55.25	4.65	4.17	2.99c	84.03	88.20	59.65
	25	12.19ab	16.11	15.57	66.07	61.58	54.70	4.34	4.20	2.41d	78.80	83.13	48.95
	50	12.34ab	15.41	15.33	65.35	62.03	54.01	4.69	3.97	1.80e	82.65	86.72	44.25
	100	11.35b	15.96	15.44	67.26	61.33	53.38	4.28	3.79	1.77e	82.58	80.61	43.23
Average mad (%)		2.03	1.26	1.55	0.87	0.79	0.93	3.08	1.19	1.06	1.13	1.87	1.14
ANOVA		P<0.05	NS	NS				NS	NS	P<0.01			
Saccharose	0	11.96	15.50	15.94	68.68	61.53	58.00	4.15	4.04	3.36a	83.46	79.36	71.12
	5	12.41	15.92	16.55	68.21	61.64	58.13	4.05	4.01	3.04a	83.21	78.53	64.89
	10	13.24	16.12	16.68	67.65	59.37	56.56	4.28	3.97	3.19a	83.28	74.41	65.28
	25	12.25	16.28	15.02	68.54	61.70	56.62	4.21	4.08	2.25b	81.44	76.15	51.60
	50	11.80	16.63	16.75	68.69	60.40	55.63	3.91	4.07	2.32b	80.39	74.09	54.65
	100	12.21	17.16	16.91	68.33	60.88	56.30	4.18	4.22	2.54b	78.23	77.44	55.32
Average mad (%)		2.25	2.02	2.85	0.51	0.98	0.70	1.58	2.18	3.33	1.20	1.84	0.57
ANOVA		NS	NS	NS				NS	NS	P<0.01			

[a] Means (two replicates), within a food component and column, followed by the same letter are not significantly different at P > 0.05 (Duncan).

[b] Average mean absolute deviation (m.a.d.) percentage of a column within a food component.

[c] Analysis of variance: NS = not significant; P<0.01 and P<0.05, significant at the 0.01 or 0.05 level of probability, respectively.

Table 2.5 Concentration[a] of linalool and E2MB in LLDPE and model solution at different concentrations of food components after 1, 5 and 14 days at 4°C.

		Linalool						E2MB					
Food	Conc.	LLDPE (mg/g)			Model solution (mg/l)			LLDPE (mg/g)			Model solution (mg/l)		
component	(g/l)	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14
ß-lg	0	0.15	0.13ab	0.18a	88.12	89.33	78.79	0.23	0.20a	0.33a	85.64	84.48	82.55
	5	0.14	0.12a	0.16ab	89.82	88.46	82.89	0.23	0.23a	0.36a	86.45	84.39	83.93
	10	0.16	0.16c	0.18a	87.98	87.51	80.12	0.37	0.38bc	0.47b	85.07	77.86	82.19
	20	0.17	0.15bc	0.17a	86.82	86.57	79.15	0.26	0.35b	0.29a	85.35	84.78	82.54
	30	0.15	0.15bc	0.17a	88.73	87.71	80.81	0.27	0.45cd	0.34a	84.88	83.77	83.72
	40	0.15	0.16bc	0.14b	87.86	86.13	80.90	0.41	0.49d	0.35a	85.74	82.87	82.20
Average mad (%)[b]		6.69	3.93	3.70	0.36	0.50	0.85	14.19	8.36	6.44	0.54	0.66	0.62
ANOVA[c]		NS	P<0.05	P<0.05				NS	P<0.01	P<0.05			
Casein	0	0.22	0.20a	0.31	88.59	86.11	80.02	0.42ab	0.39a	0.44ab	86.36	84.00	83.98
	5	0.21	0.19ab	0.23	88.59	85.38	83.91	0.48bcd	0.47b	0.50bc	86.47	84.27	85.11
	10	0.21	0.18b	0.23	89.28	86.76	83.46	0.54d	0.54c	0.56cd	89.45	87.13	85.67
	20	0.19	0.17bc	0.31	90.76	86.29	89.17	0.39a	0.37a	0.38a	86.47	83.88	84.04
	30	0.19	0.15d	0.26	89.28	87.16	85.84	0.45abc	0.40a	0.54bcd	87.42	85.71	84.64
	40	0.18	0.16c	0.28	88.53	86.83	84.55	0.52cd	0.47b	0.62d	86.57	84.26	83.28
Average mad (%)		3.74	2.47	7.96	0.48	0.73	0.48	4.26	2.50	4.36	0.25	0.55	0.58
ANOVA		NS	P<0.01	NS				P<0.05	P<0.01	P<0.01			
Pectin	0	0.16a	0.19	0.17a	90.53	89.39	92.47	0.25a	0.23a	0.28a	86.34	84.62	84.02
	5	0.20cd	0.19	0.19a	90.79	92.25	93.09	0.31a	0.29ab	0.35bc	85.06	82.71	81.61
	10	0.19bcd	0.18	0.20a	93.53	94.16	94.73	0.43b	0.40c	0.40d	87.28	84.87	81.63
	15	0.17ab	0.17	0.24b	92.16	93.14	90.70	0.27a	0.23a	0.32ab	86.33	85.34	82.12
	20	0.21d	0.19	0.25b	92.61	92.00	90.38	0.33ab	0.33bc	0.38cd	86.12	82.57	81.42
	25	0.19abc	0.21	0.26b	90.27	90.36	89.91	0.44b	0.39c	0.49e	84.80	78.62	81.00
Average mad (%)		2.41	3.53	4.71	0.51	0.94	1.41	7.59	5.11	3.21	0.64	1.00	1.30
ANOVA		P<0.05	NS	P<0.01				P<0.05	P<0.01	P<0.01			
CMC	0	0.18a	0.18	0.17	91.12	95.64	87.60	0.11a	0.26a	0.28	84.51	83.46	86.07
	5	0.22ab	0.18	0.18	91.40	93.13	94.34	0.42b	0.30ab	0.35	83.41	82.03	84.97
	10	0.24bc	0.18	0.19	92.59	92.77	94.64	0.49b	0.42cd	0.38	84.57	81.33	84.52
	15	0.26bc	0.20	0.18	91.23	95.18	94.08	0.48b	0.34abc	0.35	83.61	84.66	83.62
	20	0.25bc	0.20	0.20	89.25	93.63	92.95	0.52b	0.38bc	0.39	81.14	83.47	82.58
	25	0.28c	0.21	0.21	87.82	91.32	90.79	0.68c	0.48d	0.43	80.75	81.18	54.61
Average mad (%)		4.81	4.42	3.19	0.61	0.44	1.68	8.73	5.47	13.24	0.55	0.23	3.58
ANOVA		P<0.05	NS	NS				P<0.01	P<0.01	NS			
Lactose	0	0.23	0.21a	0.32	85.24	84.14	77.80	0.49ab	0.40a	0.35a	85.60	85.23	86.30
	5	0.24	0.20a	0.30	87.06	86.00	79.20	0.49ab	0.43ab	0.42b	84.34	82.36	84.90
	10	0.24	0.21a	0.31	87.53	87.13	79.57	0.49ab	0.48b	0.45bc	85.52	83.31	87.20
	25	0.23	0.25b	0.32	85.73	87.01	78.75	0.56bc	0.57c	0.52c	84.66	83.09	85.11
	50	0.27	0.25b	0.33	84.89	86.37	76.98	0.46a	0.49b	0.51c	84.30	82.79	85.63
	100	0.28	0.30c	0.34	86.35	85.17	76.11	0.64c	0.64d	0.64d	84.12	82.60	86.97
Average mad (%)		3.85	3.42	3.27	0.58	1.52	0.83	4.19	3.66	4.32	0.75	0.44	0.51
ANOVA		NS	P<0.01	NS				P<0.05	P<0.01	P<0.01			
Saccharose	0	0.23a	0.18a	0.18a	86.69	78.38	79.92	0.28a	0.27a	0.33a	86.09	82.96	80.54
	5	0.23ab	0.18a	0.17a	86.67	81.90	81.18	0.38ab	0.35ab	0.38a	84.38	82.31	79.72
	10	0.26b	0.18a	0.19a	85.72	80.54	79.94	0.55cd	0.39bc	0.46b	83.83	80.57	78.22
	25	0.26b	0.20ab	0.19a	86.39	81.56	79.58	0.37ab	0.38b	0.36a	84.49	82.86	77.64
	50	0.26b	0.22bc	0.23b	86.54	81.06	79.60	0.43bc	0.46c	0.50b	83.67	80.51	78.21
	100	0.30c	0.24c	0.24b	85.64	80.99	79.09	0.66d	0.59d	0.60c	82.65	80.75	77.12
Average mad (%)		2.51	3.30	4.22	0.48	1.24	0.60	8.30	5.66	4.99	0.46	0.82	0.59
ANOVA		P<0.01	P<0.01	P<0.01				P<0.01	P<0.01	P<0.01			

[a] Means (two replicates), within a food component and column, followed by the same letter are not significantly different at P > 0.05 (Duncan).
[b] Average mean absolute deviation (m.a.d.) percentage of a column within a food component.
[c] Analysis of variance: NS = not significant; P<0.01 and P<0.05, significant at the 0.01 or 0.05 level of probability, respectively.

by LLDPE, it was possible that an outlier could have caused the effect. Studying the Duncan-test results avoids making a wrong interpretation of such data. Because duplicate analysis were made, the average mean absolute deviation (mad) percentage of each exposure day was preferred to the coefficient of variation (CV).[19] In general these mad values were less than 10%.

Table 2.6 Absorption by LLDPE, recovery (LLDPE + solution) and coefficient of variation (CV) of flavour compounds by LLDPE after 1, 5 and 14 days exposure at 4°C.

	Day 1				Day 5				Day 14			
Flavour compound	LLDPE (mg/g)	CV (%)	Recovery (%)	CV (%)	LLDPE (mg/g)	CV (%)	Recovery (%)	CV (%)	LLDPE (mg/g)	CV (%)	Recovery (%)	CV (%)
Limonene (n=12)	12.14	8.9	92.1	2.8	15.34	6.2	88.8	2.8	15.67	3.6	86.0	4.7
Decanal (n=12)	4.13	8.0	101.5	2.5	3.98	6.7	98.9	3.7	3.42	10.5	82.3	8.4
Linalool (n=12)	0.20	17.9	101.8	2.5	0.18	15.4	100.4	6.7	0.22	32.1	95.4	7.3
E2MB (n=12)	0.29	45.8	99.3	0.9	0.29	29.3	97.4	1.2	0.33	21.3	97.2	2.5

Table 2.6 gives the average absorption values of limonene, decanal, linalool and E2MB by LLDPE, without addition of a food component. The total recovery of aroma compounds (model solution + LLDPE) was in the range 92-102% after 1 day of exposure, indicating that all aroma compounds had been extracted. LLDPE easily absorbed limonene; after only 5 days of exposure a level of approximately 16 mg limonene per g of LLDPE was found. Exposure for a longer time resulted only in a slight increase. Decanal was absorbed by LLDPE to a lesser extent than limonene and had reached a level of approximately 4 mg decanal per g of LLDPE after one day of exposure. After 14 days, a decrease of decanal absorption (i.e. desorption) by LLDPE took place, which was caused by a sudden decrease in the amount of decanal in the model solution (recovery 82%). This is probably due to chemical degradation of decanal, although volatile degradation products were not detected by static headspace GC analysis. Linalool and E2MB were absorbed by LLDPE in small quantities; approximately 0.20 mg linalool per gram of LLDPE and 0.30 mg E2MB per gram of LLDPE.

2.3.2 Influence of β-lactoglobulin and casein

The presence of β-lactoglobulin (β-lg) showed a significant effect ($P<0.05$) on limonene and linalool absorption by LLDPE after 5 and 14 days of exposure, but the effect did not follow a clear upward or downward trend as the Duncan-test results show. The overall effect of β-lg was very small, which means that probably no interaction occurred between β-lg and limonene or linalool. Dufour and Haertlé[20] and Charles *et al.*[21] reported that β-lg does not bind limonene and linalool, respectively.

At a concentration of 40 g/l casein, a 40% decrease of limonene absorption was observed after 1 day, which diminished to 15% after 14 days. This indicates a reversible but not strong interaction between limonene and casein. Interactions between flavour compounds and proteins have been the subject of many flavour release studies. Hansen[22] reported that two different types of interactions can occur between a protein and flavour compound. Flavour compounds can be bound loosely by an electrostatic attraction between the flavour compound and a charged location on a protein (the binding is not permanent). Alternatively, flavour compounds (aldehydes or ketones) can be tightly bound to milk proteins by chemical interaction with specific, chemical reactive amino acids within the protein, so called Schiff's base formation.

A more pronounced effect was found for decanal which showed a statistically significant ($P<0.01$) decrease of absorption into LLDPE at increasing concentrations of β-lg and casein. The binding between β-lg or casein and decanal is permanent or very strong (e.g. covalent), because no substantial increase of absorption took place after prolonged storage. However, after 14 days of exposure a sudden decrease of decanal absorption in LLDPE was observed at a β-lg and casein concentration of 5 g/l, which was followed by an increase again at higher protein concentrations (see Figure 2.2). Apparently, a desorption of decanal from the LLDPE film to the protein model solutions took place. The amount of free decanal in the model solution (determined with static headspace analysis) was also decreased, which means that decanal was bound by β-lg (at 5 and 10 g/l) and casein during storage. Damodaran[23] reported that binding of aldehydes by proteins could be so strong that solvents could not extract them. Landy *et al.*[24] reported that binding of ligands to hydrophobic regions of soy proteins caused protein unfolding, creating new binding sites. Heating of proteins has a similar effect on the number of binding sites.[22] An explanation of the increased absorption after 14 days at higher concentrations (>5 g/l) could be the decrease of available binding sites. Bakker[25] and Landy

et al.[24] also found that an increasing protein concentration (>2% w/w) reduced the number of binding sites, probably due to protein-protein interactions.

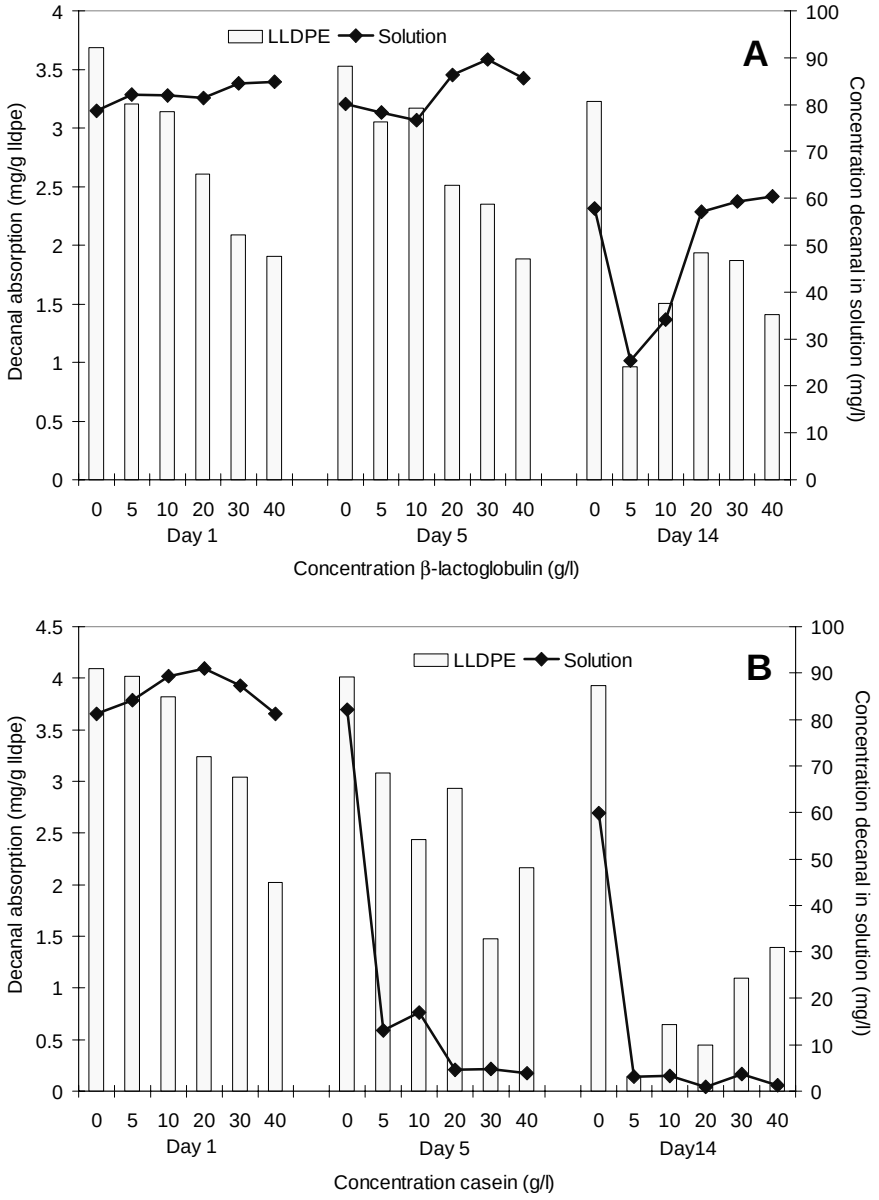

Figure 2.2 Absorption of decanal by LLDPE at different concentrations of β-lactoglobulin (A) and casein (B) after 1, 5 and 14 days of exposure at 4°C.

The absorption curves of E2MB followed a (strange) zigzag pattern throughout the 14 days of storage. This pattern was not unique for protein model solutions only, but all investigated food components showed similar results for E2MB (food component independent). Up to concentrations of 10 g/l absorption increased, probably due to a concentration or 'salting out' effect (loss of free water) of the less apolar E2MB. At a concentration of the different food components of approximately 10-15 g/l a sudden decrease of absorption took place, followed

by a further increase at higher concentrations. However, static headspace analysis did not show a detectable decrease in the amount of free E2MB for any of the studied food components. The behaviour of E2MB in this situation cannot be fully explained and requires further investigations.

2.3.3 Influence of pectin and CMC

Increasing concentrations of pectin and CMC showed a significant ($P<0.01$) effect on the absorption of limonene by LLDPE. After one day of exposure absorption decreased by 50% at 25 g/l pectin or CMC. Since pectin and CMC are generally regarded as thickening agents, their effect on the absorption of limonene by LLDPE may be due to increased viscosity. Baines and Morris[26] concluded that flavour release was unaffected by disordered polysaccharides at concentrations below coil overlap, but decreased sharply at higher concentrations. The coil overlap value, C*, is a characteristic concentration for disordered or 'random coil' polymer systems, in which individual polymer coils begin to overlap. This value is determined by noting the sharp break when concentration is plotted on a logarithmic scale against specific viscosity, as measured by rotational viscometers. In Figure 2.3, relative absorption S_x/S_0 (Sorption at X g/l / Sorption at 0 g/l) of limonene and specific viscosity η_{sp} is plotted against pectin and CMC concentration C, respectively. The best fit of the tangents in Figure 2.3 was determined using linear regression analysis, resulting in a coil overlap value of C*=6 g/l for pectin as well as for CMC. At concentrations below C*, at which levels individual polymer chains are free to move independently, relative absorption decreased slightly or remained relatively constant. At concentrations higher than C*, levels at which chains interpenetrate and generate a network, relative absorption decreased rapidly because diffusion of flavour molecules from within the solution to the surface of the plastic film was reduced (inhibition of surface replenishment).

In Figure 2.4, specific viscosity is plotted against relative absorption of limonene, which shows that pectin and CMC solutions of similar viscosity did not have the same absorption suppression, suggesting that binding interactions might be present. Roberts *et al.*[27] also reported that thickened solutions of similar viscosity did not show the same flavour release. Their results showed an influence of both viscosity and binding interactions with the

thickener on the release of flavour. Binding interactions with carbohydrate-based thickeners are often due to adsorption, entrapment in microregions, complexation, encapsulation and hydrogen bonding between appropriate functional groups.[17,28] Figure 2.3 shows that these

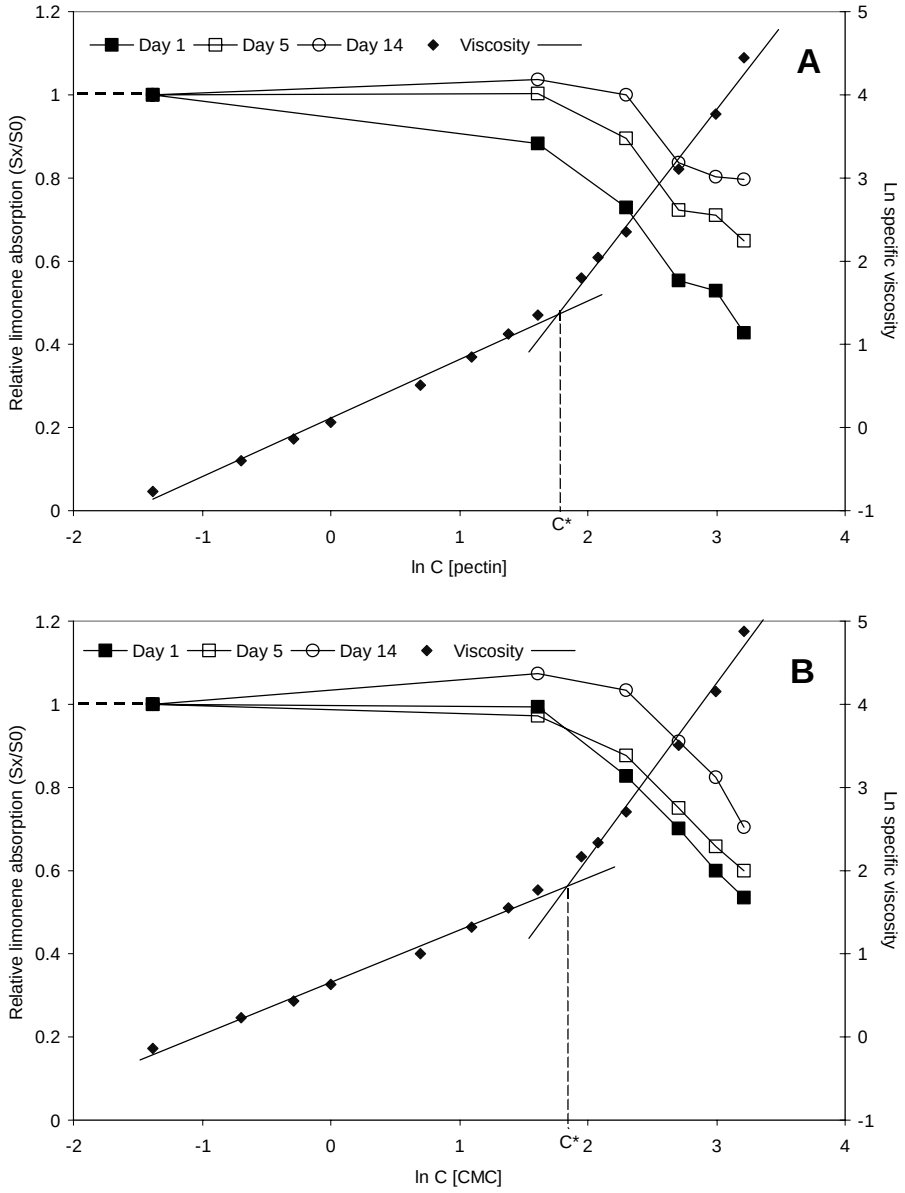

Figure 2.3 Influence of specific viscosity of pectin (A) and CMC (B) model solutions on the relative absorption of limonene by LLDPE after 1, 5 and 14 days of exposure at 4°C.

interactions were reversible, because the amount of absorption increased until an equilibrium was reached. Absorption of decanal by LLDPE was also significantly reduced by 12-25% with increasing concentrations of pectin and CMC after 1 and 5 days of exposure. After 14 days of exposure a significant effect on the level of pectin was indicated, although Duncan-test results did not show a clear trend. However, CMC had a decreasing effect on the

absorption of decanal after 14 days of exposure. A decrease of free decanal by 25-35% in the model solution caused a desorption of absorbed decanal from LLDPE to the model solution.

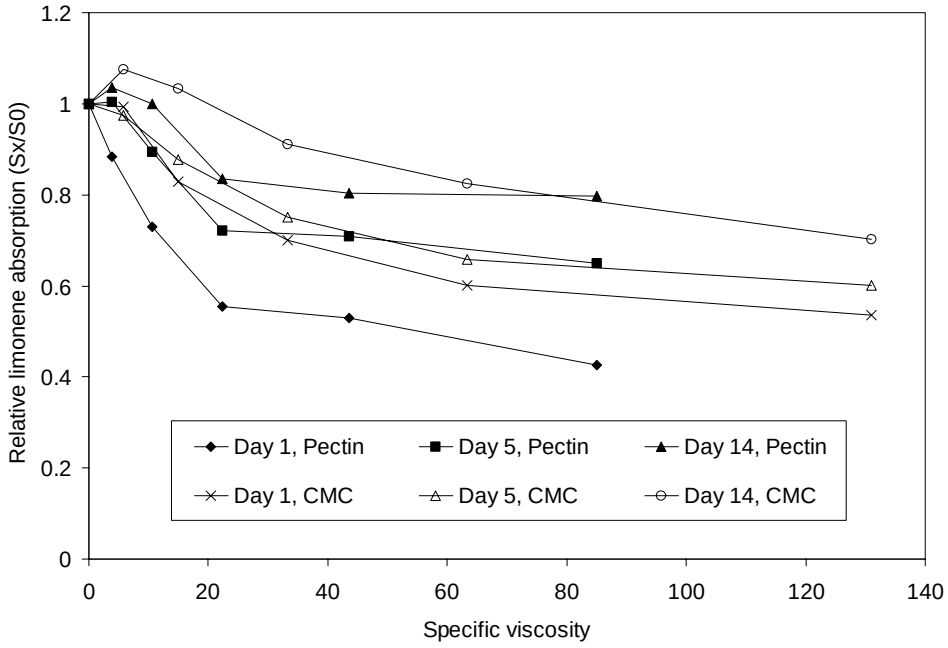

Figure 2.4 Influence of specific viscosity on relative absorption of limonene by LLDPE after 1, 5 and 14 days of exposure at 4°C.

A possible explanation will be given in the next section describing the influence of lactose and saccharose. The effect of pectin and CMC on the absorption of linalool is not quite clear. There is a tendency for absorption to increase due to a salting out effect at higher concentrations of thickener.

2.3.4. Influence of lactose and saccharose

Lactose and saccharose showed no significant effect on the absorption of limonene by LLDPE. The absorption of decanal was also not affected by lactose and saccharose up to 5 days of exposure, but decreased significantly ($P<0.01$) after 14 days of exposure. The amount of free decanal in the lactose- and saccharose model solutions (100 g/l) dropped by 40% and 25%, respectively, resulting in a desorption of absorbed decanal. A similar sudden decrease of free decanal in the model solution after 14 days was also found for CMC model solutions. Nawar[29] has described a depression in the headspace concentration of 2-heptanone and heptanal with increasing sucrose concentrations (0-60%). It appeared that the decrease in

headspace concentration did not involve a direct interaction between sugar and volatile, but rather occurred via an interaction of the sugar with the water molecules. Reineccius *et al.*[30] found a decrease of limonene and cymene (no aldehydes were studied) with increasing sucrose concentrations (0-10%) at 20°C. They suggested that this was probably caused by a catalyst, which could have triggered a complex chain reaction between sugars and volatiles. Roberts *et al.*[27] suggested that inclusion complexes might be present in concentrated sucrose solutions for hydrophobic molecules, which results in a greater depression of volatility by sucrose. In the present study there might also be an interaction effect between a sugar and decanal. Absorption of linalool by LLDPE increased with increasing concentrations of saccharose and showed a trend to increase further with higher concentrations of lactose. Disaccharides can lower the amount of bulk water due to hydration, which increases the effective concentration of some volatile compounds[31] and therefore can enhance their absorption.

2.4 Conclusion

Absorption of flavour compounds by LLDPE is complex and several factors play an important role. Flavours may be dissolved, adsorbed, bound, entrapped, encapsulated or diffusion limited by food components. Proteins and carbohydrates interact with flavours, changing the concentration of free flavour in the solution and consequently increasing or decreasing the amount of absorption. The polarity of a flavour compound determines not only the amount of absorption by LLDPE, but also the interaction with food components. β-lg and casein are able to bind flavours, especially aldehydes, temporarily or permanently by hydrophobic or covalent interactions, resulting in suppression of flavour absorption by LLDPE. Polysaccharides, such as pectin and CMC, can increase viscosity and interact with flavour compounds, reducing diffusion of flavour compounds from the food matrix to the plastic film. Lactose and saccharose are able to bind water and cause a salting out effect of the less apolar flavour compounds, linalool and E2MB, resulting in an increased absorption. Storage time showed not only an important factor in reaching absorption equilibrium, but also in the time-dependent interactions between flavour compounds and food components (such as unfolding of proteins and chemical reactions with sugar-residues).

In real food products, concentrations of flavour compounds are usually substantially lower than the concentrations investigated in this study. It can be expected that a relatively larger amount of flavour compounds will interact with food components, which will suppress flavour absorption even to a larger extent. Because many food products are based on emulsions, the influence of oil and real food products on the absorption of flavour compounds by LLDPE will be investigated in a further study.

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3

Influence of food matrix on absorption of flavour compounds by linear low-density polyethylene: oil and real food products

Abstract

The influence of oil and food components in real food products on the absorption of four flavour compounds (limonene, decanal, linalool and ethyl 2-methylbutyrate) into linear low-density polyethylene (LLDPE) was studied by using a Large Volume Injection GC 'in vial' extraction method. Model food systems and real food products investigated included oil/water emulsions, oil/casein models, oil/pectin models, skim milk and whole milk. A small amount of oil (50 g/l) had a major influence on the amount of flavour absorption. Because of solubilisation of the more apolar flavour compounds limonene, decanal and linalool into the oily phase, only the remaining flavour compounds in the aqueous phase were available for absorption by LLDPE. After 14 days of exposure, absorption of limonene and decanal decreased by 97%, and that of linalool by 86%. Due to a salting out effect, absorption of the less apolar ethyl 2-methylbutyrate (E2MB) first increased with increasing oil concentration, but decreased at higher oil concentrations (> 2.5 g/l). Oil/casein and oil/pectin models showed that the more apolar flavour compounds were mainly dissolved in the oily phase and that the compounds present in the aqueous phase could interact with casein or pectin. Oil influenced the level of flavour absorption by LLDPE to a much higher extent than pectin or casein. However, the low amount of fat (1.11 g/l) in skim milk had no influence on the absorption of flavour compounds. Only the proteins in skim milk (especially casein) decreased the absorption of limonene and decanal, because the fat was probably entrapped. Whole milk, which contained a higher concentration of (free) fat, suppressed the absorption of all flavour compounds by LLDPE to the same extent as was found for the oil model solutions. In general, absorption results from skim milk and whole milk were in good agreement with the results of the investigated model solutions containing individual food components.

This chapter has been published as:

Van Willige RWG, Linssen JPH and Voragen AGJ, *J Sci Food Agric* **80:**1790-1797 (2000).

3.1 Introduction

In a previous paper[1] (Chapter 2), we discussed the influence of proteins and carbohydrates on the absorption of flavour compounds by linear low-density polyethylene (LLDPE). Proteins and carbohydrates were able to interact (direct or indirectly) with flavour compounds, changing the flavour concentration in the aqueous phase. To re-establish equilibrium between aqueous phase and plastic film, absorbed flavour compounds desorbed from LLDPE. The composition of a food matrix is of great importance (besides other factors - see Figure 3.1) in determining the amount of flavour absorption by plastic packaging materials.

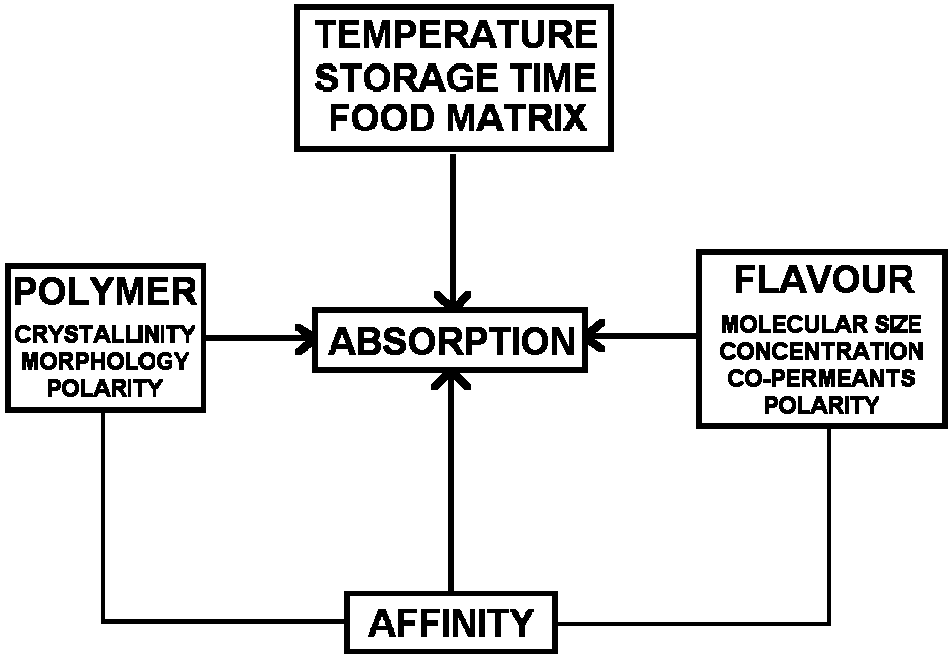

Figure 3.1 Factors influencing flavour absorption by plastic polymers.

Because many food products are emulsions of fat and water, such as milk and milk products, the fat content is an important variable in the food matrix. Fat/oil content is often reduced in order to decrease calorific intake to make food healthier. Removal or reduction of lipids can lead to an imbalanced flavour, often with a much higher intensity than the original full fat food.[2,3] De Roos[4] reported that in products containing aqueous and lipid phases, a flavour compound is distributed over three phases: fat (or oil), water, and air. Flavour release from the oil/fat phase of a food proceeded at a lower rate than from the aqueous phase. This was attributed, first to the higher resistance to mass transfer in fat and oil than in water and,

second to the fact that in oil/water emulsions flavour compounds had initially to be released from the fat into the aqueous phase before they could be released from the aqueous phase to the headspace. Kinsella[5] reported that several mechanisms might be involved in the interaction of flavour compounds with food components. In lipid systems, solubilization and rates of partitioning control the rates of release. Polysaccharides can interact with flavour compounds mostly by non-specific adsorption and formation of inclusion compounds. In protein systems, adsorption, specific binding, entrapment, encapsulation and covalent binding may account for the retention of flavours.

Oil and fatty acids can also be absorbed by polymers[6,7] resulting in increased oxygen permeability[8] and delamination of laminated packaging material.[9,10] However, the availability of data about the influence of oil on the absorption of flavour compounds by plastic packaging materials is limited. Nielsen *et al.*[11] found that some apple aroma compounds added to and stored in pure olive oil were lost to a greater extent to LDPE than from an aqueous solution, probably due to differences in polarity of the aromas, polymer and solutions.

Thus, oil/fat has a major influence on flavour compounds (perception, intensity, volatility, etc.) and on the properties of packaging material. In this paper, the influence of an oily matrix on the absorption of flavour compounds by LLDPE was investigated. The effects of individual food components on flavour absorption by LLDPE found in this study were compared with absorption data of real food products and model solutions with a more complex matrix.

3.2 Materials and methods

3.2.1 Materials

Linear low-density polyethylene (LLDPE) film, thickness 50 μm and density 925 kg/m^3, was manufactured at Dow Benelux N.V. (Terneuzen, The Netherlands). The flavour compounds, ethyl 2-methylbutyrate (E2MB) and linalool were purchased from Acros, decanal from Merck and (+)-limonene from Sigma. The solubility in water at 25°C of limonene, decanal, linalool and E2MB is 0.0027, 0.012, 0.11 and 2.47 g/l and their hydrophobicity (Log P) is 4.58, 4.09, 3.28 and 2.12, respectively.[12] Log P represents the hydrophobicity: the higher Log

P, the more hydrophobic a compound. Flavour compounds were added to all model solutions with a Micropipette (Socorex, Lausanne, Switzerland), giving a final concentration of 83 mg/ of decanal, 84 mg/l of limonene, 87 mg/l of E2MB and 87 mg/l of linalool. Tween 80 from Merck was used as an emulsifier.

The non-volatile components used were: oil (ESTASAN 3575 GTCC 60, glycerol tricaprylate C8 (55%) / glycerol tricaprate C10 (45%)) from Unichema International (Barcelona, Spain); whole milk (UHT) from a local store, containing 36 g/l of fat, 32,5 g/l of protein and 46 g/l of lactose determined with a Milko-Scan 134 A/B (N.Foss Electric, Hilleröd, Denmark); low heat spray-dried skim milk powder (Nilac) from NIZO (Ede, The Netherlands), containing 520 g/kg of lactose, 360 g/kg of protein, 80 g/kg of ashes, 30 g/kg of water and 10 g/kg of fat; casein (bovine milk, 88% protein) from Sigma and pectin (GENU beta pectin; DE 57% and DA 23%) from Hercules (Barneveld, The Netherlands).

3.2.2 Preparation of oil model solutions

Oil model solutions were prepared in stoppered conical flasks by mixing calculated amounts of oil with water and Tween 80. All model solutions contained 4 g/l of Tween 80 and had concentrations of 0, 0.5, 1.5, 2.5, 5.0, 10.0, 20.0 and 50.0 g/l oil. An Ultra Turrax T25 (IKA-Labortechnik, Staufen, Germany) was used for homogenization for 2 minutes at 9500 rpm. After adding the flavour compounds, model solutions were equilibrated overnight at 4°C using a magnetic stirrer.

3.2.3 Preparation of pectin/oil and casein/oil model solutions

Pectin/oil and casein/oil model solutions were prepared in two stages. A mixture of Tween 80 and oil was diluted under continuous stirring by slowly adding water to a concentration of 8 g/l of Tween 80 and 3 g/l of oil. Stock solutions of pectin and casein were prepared at concentrations of 0, 10, 20, 30 and 40 g/l and 0, 10, 20, 40, 60 and 80 g/l, respectively. The final model solutions were prepared in stoppered conical flasks by adding 100 ml of the Tween/oil stock solution to 100 ml of the pectin or casein stock solutions. All final model solutions contained 4 g/l of Tween 80, 1.5 g/l of oil and 0, 5, 10, 20, 30 and 40 g/l of casein

or 0, 5, 10, 15, 20 and 25 g/l of pectin. After homogenization of the model solutions with an Ultra Turrax T25 for 2 minutes at 9500 rpm, flavour compounds were added and subsequently equilibrated overnight at 4°C using a magnetic stirrer.

3.2.4 Milk sample preparations

Milk model solutions were prepared in stoppered conical flasks by mixing calculated amounts of skim milk powder or whole milk with water and Tween 80. All model solutions contained 4 g/l of Tween 80 and were prepared with boiled demi water, which was cooled to room temperature before use. Skim milk model solutions contained 0, 5, 10, 20, 30, 40 g/l of protein and 0, 0.14, 0.28, 0.56, 0.83, 1.11 g/l of fat. The six whole milk model solutions contained 0, 2.5, 5.0, 10.0, 20.0, 32.5 g/l of protein and 0, 2.8, 5.5, 11.1, 22.2, 36.0 g/l fat. After adding the flavours, model solutions were equilibrated overnight at 4°C using a magnetic stirrer.

3.2.5 Exposure and extraction conditions

Strips of LLDPE (1.5 x 2.0 cm, 13.9 ± 0.1 mg) were individually placed into 15-ml Teflon screw cap vials (Supelco), and fully immersed in the model solution (15 ml). Samples were stored in the dark at 4°C for 1, 5 and 14 days. No changes in pH and colour were observed in the model solutions during storage. Model solution and strips were analysed with a static headspace GC and a Large Volume Injection GC (LVI-GC) 'in vial' extraction method, respectively. GC conditions and extraction method have been described previously.[1]

3.2.6 Statistical analysis

All determinations were carried out in duplicate. Data were subjected to one-way analysis of variance (ANOVA) with concentrations of a food component as the main effect. Differences between concentrations of a food component were tested by means comparison with the Duncan test when ANOVA was significant ($P<0.05$).

3.3 Results and discussion

Table 3.1 and 3.2 set out the absorption values (mg/g LLDPE) of limonene, decanal, linalool and E2MB by LLDPE after 1, 5 and 14 days of exposure at 4°C.

Table 3.1 Concentration[a] of limonene and decanal in LLDPE and model solution at different concentrations of food components after 1, 5 and 14 days at 4°C.

		Limonene						Decanal					
Food	Conc.	LLDPE (mg/g)			Model solution (mg/l)			LLDPE (mg/g)			Model solution (mg/l)		
component	(g/l)	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14
Oil	0.0	13.33a	13.72a	14.25a	65.47	59.71	65.08	4.70a	4.18a	2.68a	79.24	75.56	67.04
	0.5	8.99b	9.42b	9.66b	73.01	70.51	75.02	3.03b	2.73b	1.89b	83.15	78.68	74.21
	1.5	5.51c	5.56c	5.73c	75.88	77.52	79.97	1.90c	1.74c	1.29c	83.40	83.69	79.12
	2.5	4.15d	3.90d	3.73d	79.07	80.36	82.73	1.48d	1.27d	0.96d	83.34	81.85	80.50
	5.0	2.32e	2.12e	2.35e	81.60	81.03	84.41	0.88e	0.80e	0.57e	88.54	83.16	83.61
	10.0	1.27f	1.20f	1.41f	82.72	81.88	85.42	0.50ef	0.47f	0.38f	78.75	77.79	76.77
	20.0	0.67f	0.65g	0.65g	83.34	82.17	85.26	0.27f	0.24g	0.17g	91.10	81.47	82.94
	50.0	0.50f	0.27g	0.27g	83.75	82.32	84.46	0.21f	0.10h	0.06g	88.93	88.73	82.29
Average mad (%)[b]		6.87	2.44	1.71	0.41	0.44	0.76	7.51	4.44	3.11	1.71	1.40	1.84
ANOVA[c]		P<0.01	P<0.01	P<0.01				P<0.01	P<0.01	P<0.01			
Pectin in	0.0	4.38a	5.13a	4.97a	75.71	73.96	72.06	1.41ab	1.92	0.99	82.45	83.25	65.06
1.5 g/l oil	5.0	3.93b	5.36a	5.47b	76.53	75.73	74.14	1.27a	1.52	0.95	74.47	69.62	55.05
	10.0	2.78c	4.58b	5.42b	78.36	76.35	73.31	1.22a	1.31	0.73	76.92	72.47	54.83
	15.0	2.54c	4.10b	4.86a	81.14	78.06	73.30	1.47ab	1.58	0.71	79.24	74.79	46.83
	20.0	2.82c	4.27b	4.71a	78.42	76.12	72.46	1.68b	1.75	0.89	78.90	76.64	50.44
Average mad (%)		2.34	2.78	1.73	0.47	0.56	0.72	4.18	5.36	24.98	0.77	0.49	8.67
ANOVA		P<0.01	P<0.01	P<0.01				P<0.05	NS	NS			
Casein in	0.0	4.96a	5.52	4.93	77.74	76.35	77.08	1.97a	1.91	1.30a	83.55	82.30	66.06
1.5 g/l oil	5.0	4.47ab	5.06	5.49	78.71	79.82	76.62	1.77ab	1.48	0.00b	83.96	74.78	2.06
	10.0	4.23bc	5.24	4.91	78.24	77.66	75.56	1.64bc	1.66	0.00b	81.21	74.83	0.97
	20.0	4.20bc	4.86	5.09	79.08	79.14	77.32	1.60bc	1.60	0.00b	81.26	67.84	0.75
	30.0	3.89cd	4.69	4.72	79.30	79.31	76.39	1.64bc	1.53	0.00b	80.89	64.82	0.93
	40.0	3.58d	4.88	4.83	79.23	78.83	77.00	1.46c	1.40	0.29b	80.89	46.17	18.64
Average mad (%)		3.38	2.97	2.77	0.38	0.69	0.53	3.43	8.52	16.98	0.72	2.38	15.57
ANOVA		P<0.01	NS	NS				P<0.05	NS	P<0.01			
Protein/fat	0.0/0.00	13.34a	16.73a	17.42a	66.08	63.43	61.59	4.70a	4.53a	3.73a	79.84	81.13	72.97
in	5.0/0.14	12.88a	16.19b	16.56ab	65.08	64.90	60.52	4.05b	3.45b	0.60bc	75.38	71.95	7.31
skim milk	10.0/0.28	11.32b	15.96b	15.93b	68.22	66.27	62.37	3.36c	3.01c	0.26d	77.65	70.76	2.61
	20.0/0.56	10.06c	13.38c	12.39c	70.56	69.01	64.10	2.80d	2.14d	0.47cd	74.09	63.85	4.89
	30.0/0.83	9.22d	11.97d	11.63cd	72.40	69.42	66.65	2.57d	1.93de	0.78b	73.86	59.74	10.53
	40.0/1.11	8.34e	11.63d	10.96d	69.95	71.07	68.12	2.29e	1.76e	0.52c	75.77	65.39	9.03
Average mad (%)		1.25	1.23	1.60	1.73	1.14	1.57	1.37	2.43	6.77	1.23	3.99	22.30
ANOVA		P<0.01	P<0.01	P<0.01				P<0.01	P<0.01	P<0.01			
Protein/fat	0.0/0.0	11.03a	15.39a	16.29a	67.62	62.47	61.35	4.10a	4.19a	3.93a	76.53	76.29	72.72
in	2.5/2.8	3.57b	4.76b	5.07b	81.13	79.71	77.75	1.77b	2.05b	1.44b	85.38	79.37	65.98
whole milk	5.0/5.5	2.36c	2.60c	3.02c	80.73	79.82	78.86	1.18c	1.22c	0.03c	81.81	79.37	8.59
	10.0/11.1	1.26d	1.53cd	1.53d	83.06	82.02	81.28	0.81cd	0.72d	0.41d	83.77	74.64	43.89
	20.0/22.2	0.68d	0.78d	0.84e	83.46	82.15	81.11	0.40de	0.42de	0.21cd	85.80	79.46	40.98
	32.5/36.0	0.41d	0.46d	0.53f	84.24	83.38	81.94	0.13e	0.31e	0.12c	86.03	78.49	34.75
Average mad (%)		3.55	2.55	2.06	0.55	0.45	0.58	5.66	7.66	11.86	4.14	3.03	11.94
ANOVA		P<0.01	P<0.01	P<0.01				P<0.01	P<0.01	P<0.01			

[a] Means (two replicates), within a food component and column, followed by the same letter are not significantly different at P > 0.05 (Duncan).
[b] Average mean absolute deviation (m.a.d.) percentage of a column within a food component.
[c] Analysis of variance: NS = not significant; P<0.01 and P<0.05, significant at the 0.01 or 0.05 level of probability, respectively.

Absorption of flavour compounds by the edges of the strips (edge absorption) was assumed constant for all samples. Because of duplicate analysis, the average mean absolute deviation (mad) percentage of each exposure day was preferred to the coefficient of variation (CV).[13] In general these mad values were less than 10%.

Table 3.2 Concentration[a] of linalool and E2MB in LLDPE and model solution at different concentrations of food components after 1, 5 and 14 days at 4°C.

		Linalool						E2MB					
Food	Conc.	LLDPE (mg/g)			Model solution (mg/l)			LLDPE (mg/g)			Model solution (mg/l)		
component	(g/l)	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14	Day 1	Day 5	Day 14
Oil	0.0	0.19a	0.16a	0.15a	89.07	84.58	93.47	0.31ac	0.19a	0.22a	85.10	82.99	88.91
	0.5	0.16ab	0.16a	0.12b	89.69	87.04	92.51	0.36ab	0.27b	0.33b	85.09	83.19	88.55
	1.5	0.14b	0.13b	0.10c	88.71	91.54	92.34	0.36ab	0.30bc	0.36b	83.85	83.75	87.79
	2.5	0.13bc	0.11c	0.08d	87.69	89.25	90.09	0.39b	0.33c	0.22a	84.27	84.51	87.91
	5.0	0.10cd	0.08d	0.07de	90.94	91.02	93.42	0.24cd	0.15ad	0.25a	84.41	83.40	87.67
	10.0	0.08de	0.07e	0.06e	89.22	89.63	91.67	0.20de	0.15ad	0.25a	86.28	84.31	89.29
	20.0	0.05f	0.05f	0.04f	90.46	88.79	90.11	0.13ef	0.12d	0.13c	85.62	85.42	89.91
	50.0	0.05ef	0.03g	0.02g	90.71	89.19	88.11	0.11f	0.07e	0.06d	82.35	83.56	88.14
Average mad (%)[b]		5.67	2.16	6.01	0.85	1.10	0.81	7.82	7.39	4.30	0.82	0.54	0.62
ANOVA[c]		P<0.01	P<0.01	P<0.01				P<0.01	P<0.01	P<0.01			
Pectin in	0.0	0.05a	0.09	0.07a	84.59	88.82	88.08	0.19a	0.27a	0.22a	85.53	83.11	83.36
1.5 g/l oil	5.0	0.06a	0.09	0.08bc	87.82	93.16	91.89	0.28b	0.38b	0.30bc	86.73	86.63	86.43
	10.0	0.07a	0.10	0.09c	88.83	91.75	89.16	0.11c	0.26a	0.34c	85.69	84.81	84.05
	15.0	0.06a	0.08	0.07ab	89.77	92.89	92.85	0.13ac	0.28a	0.28b	87.04	85.97	83.98
	20.0	0.11b	0.09	0.07ab	85.96	91.01	88.31	0.40d	0.39b	0.31bc	82.40	82.22	81.62
Average mad (%)		4.92	9.23	4.27	1.61	0.66	0.86	9.53	7.53	4.77	0.65	0.63	0.94
ANOVA		P<0.01	NS	P<0.05				P<0.01	P<0.05	P<0.05			
Casein in	0.0	0.11	0.11	0.08a	88.64	92.91	93.11	0.29a	0.32ab	0.23a	85.96	84.52	86.18
1.5 g/l oil	5.0	0.10	0.09	0.04b	89.37	93.30	94.50	0.31ab	0.33ab	0.32b	85.45	86.82	82.92
	10.0	0.10	0.11	0.03b	88.79	93.80	94.54	0.33ab	0.39bc	0.32b	84.55	83.61	81.34
	20.0	0.11	0.10	0.04b	88.54	93.19	94.44	0.33ab	0.26a	0.28ab	85.31	86.56	85.17
	30.0	0.12	0.10	0.05b	88.17	92.41	93.25	0.37bc	0.31ab	0.30b	85.46	86.46	83.61
	40.0	0.11	0.11	0.08a	87.55	92.68	95.18	0.43c	0.42c	0.42c	85.13	85.02	84.00
Average mad (%)		4.06	5.54	8.13	0.84	0.54	0.32	5.97	4.64	4.78	0.51	0.84	0.64
ANOVA		NS	NS	P<0.01				P<0.05	P<0.05	P<0.01			
Protein/fat	0.0/0.00	0.18a	0.18ab	0.20a	87.89	92.48	87.56	0.29a	0.34a	0.34	87.57	86.78	87.06
in	5.0/0.14	0.19ab	0.18a	0.17b	88.74	90.07	86.17	0.34a	0.40b	0.38	83.95	85.35	83.28
skim milk	10.0/0.28	0.18a	0.19bc	0.17b	93.64	93.34	88.09	0.37ab	0.50c	0.49	84.53	84.64	82.51
	20.0/0.56	0.19ab	0.20c	0.17b	90.38	92.80	86.93	0.44bc	0.41b	0.29	84.47	84.18	81.99
	30.0/0.83	0.21c	0.20c	0.18ab	91.19	86.50	87.21	0.52cd	0.46c	0.44	84.61	84.04	80.91
	40.0/1.11	0.20bc	0.20c	0.17b	91.17	91.39	88.17	0.59d	0.57d	0.43	80.02	83.68	80.35
Average mad (%)		1.90	1.50	2.50	0.64	1.95	0.97	5.67	2.54	7.22	1.34	0.78	1.77
ANOVA		P<0.05	P<0.05	P<0.05				P<0.01	P<0.01	NS			
Protein/fat	0.0/0.0	0.16a	0.14a	0.20a	86.30	90.35	92.78	0.18ac	0.40a	0.32a	86.32	86.82	84.77
in	2.5/2.8	0.05b	0.05b	0.16b	88.00	91.70	93.69	0.24ab	0.42a	0.36b	85.95	86.59	82.95
whole milk	5.0/5.5	0.04bc	0.03c	0.11c	88.08	92.21	93.61	0.30b	0.30b	0.35ab	84.42	83.41	83.39
	10.0/11.1	0.02cd	0.00d	0.09d	87.44	90.17	92.15	0.18ac	0.28b	0.20c	86.53	85.54	84.69
	20.0/22.2	0.00d	0.00d	0.06e	88.80	89.30	92.64	0.15ac	0.16c	0.17c	86.46	85.38	82.86
	32.5/36.0	0.00d	0.00d	0.05f	88.40	89.91	91.82	0.12c	0.13c	0.15d	86.39	86.38	83.11
Average mad (%)		6.86	2.20	2.58	2.05	1.30	1.64	10.65	3.60	3.73	0.26	0.50	0.88
ANOVA		P<0.01	P<0.01	P<0.01				P<0.05	P<0.01	P<0.01			

[a] Means (two replicates), within a food component and column, followed by the same letter are not significantly different at P > 0.05 (Duncan).
[b] Average mean absolute deviation (m.a.d.) percentage of a column within a food component.
[c] Analysis of variance: NS = not significant; P<0.01 and P<0.05, significant at the 0.01 or 0.05 level of probability, respectively.

3.3.1 Influence of oil

Table 3.1 and 3.2 show that a small amount of oil substantially affects absorption of all flavour compounds by LLDPE. Absorption of limonene, decanal and linalool was significantly ($P<0.01$) decreased although the E2MB absorption first showed an increase but then decreased at higher concentrations of oil. After 1 day of exposure and in the presence of 50 g/l of oil, limonene and decanal absorption was decreased by more than 95% and linalool by approximately 75%. In Figure 3.2, the relative absorption S_x/S_0 (Sorption at X g/l / Sorption at 0 g/l) of all flavour compounds by LLDPE is plotted against oil concentration.

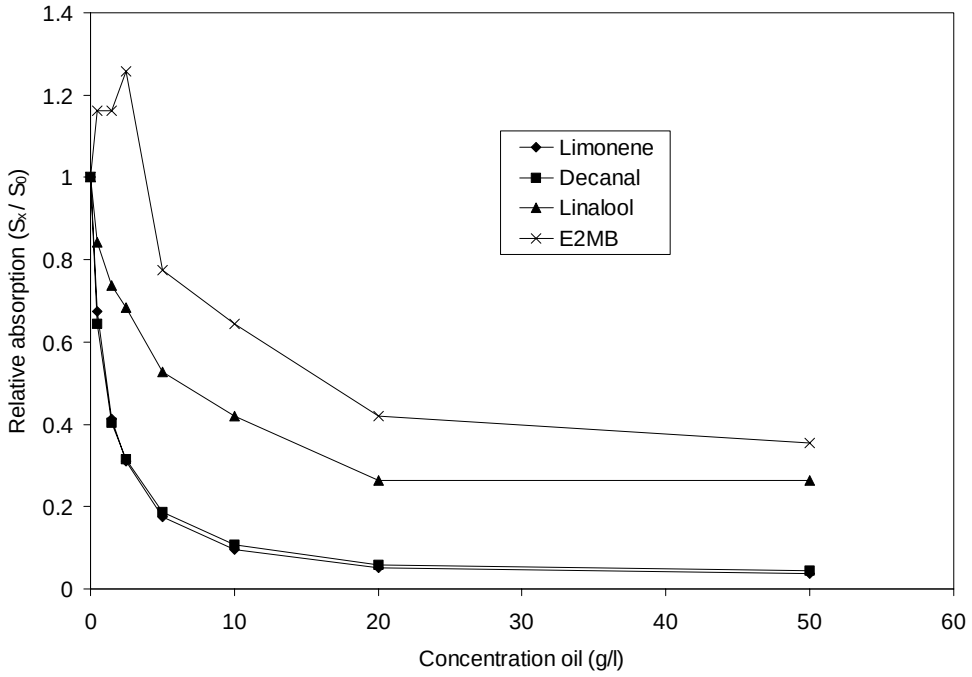

Figure 3.2 Influence of oil on the relative absorption of limonene, decanal, linalool and E2MB by LLDPE after 1 day of exposure at 4°C.

Absorption of flavour compounds was affected by oil concentration in the following order: limonene and decanal > linalool > E2MB. Because limonene and decanal are more soluble in the oily phase than in the aqueous phase, an increasing oil content resulted in an increased amount of these compounds in the oily phase. Consequently, the amount of these flavour compounds in the aqueous phase and LLDPE will decrease. Due to their somewhat higher polarity, relative absorption of linalool and E2MB was less affected by the presence of oil. At low concentrations of oil, E2MB was probably displaced from the oily phase by the more apolar flavour compounds, limonene and decanal. Consequently, the concentration of E2MB in the aqueous phase increased, resulting in an increased absorption of E2MB by LLDPE. At

higher oil concentrations, enough oil was available to solve E2MB, resulting in a decreased E2MB absorption.

Figure 3.3 shows that in the presence of oil, no substantial increase of limonene absorption took place after the first day of exposure. Obviously, oil is capable of retaining limonene very well, ie the oil/water partition coefficient is high.

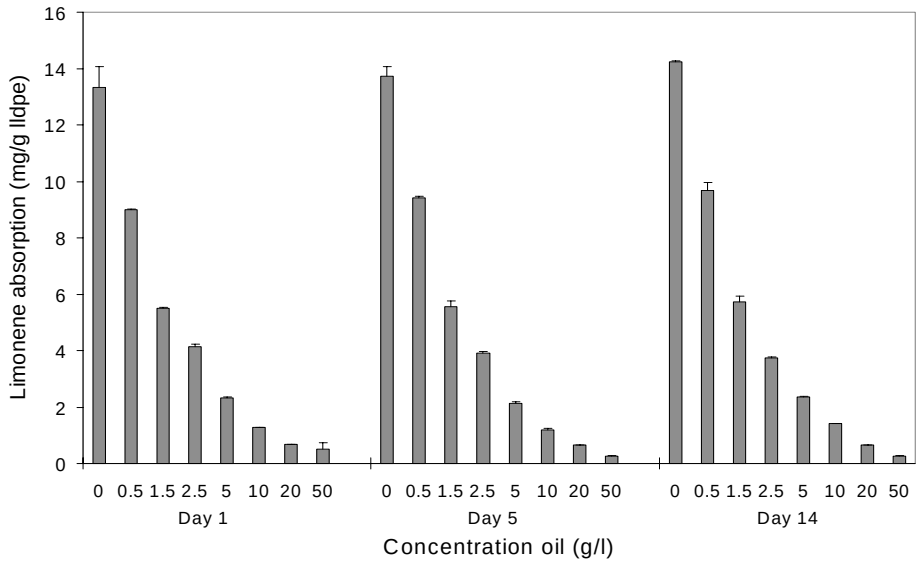

Figure 3.3 Influence of oil on the absorption of limonene by LLDPE after 1, 5 and 14 days of exposure at 4°C.

On a molecular level, triglycerides lower the vapour pressure of lipophilic flavour compounds. This is an important effect since most flavour compounds are lipophilic. Factors influencing this effect include: (1) physical form (oil has a greater effect than solid fat); (2) distribution (emulsified versus not emulsified); (3) temperature, especially near the melting point of the fat; (4) fatty-acid chain length (less effect for a given flavour compound as fatty-acid chain length increases); and (5) degree of unsaturation (greater effect for a given flavour compound as fat unsaturation increases).[14] In general, very small amounts of oil added to an aqueous system can significantly decrease the absorption of flavour compounds by LLDPE.

3.3.2 Influence of a mixture of oil and pectin or casein

To investigate the influence of a matrix consisting of two food components, model solutions with a fixed concentration of oil (1.5 g/l), and a variable concentration of pectin or casein were prepared. In a previous study[1] (Chapter 2), increasing the concentration of pectin (0 to

20 g/l) and casein (0 to 40 g/l) resulted in a decrease of limonene absorption from 12.14 to 6.43 mg/g LLDPE and 13.00 to 7.26 mg/g LLDPE, respectively, after 1 day of exposure. Table 3.1 shows that addition of oil (1.5 g/l) to these model solutions resulted in a limonene absorption of 4.38 to 2.82 mg/g LLDPE for the pectin/oil model solutions and 4.96 to 3.58 mg/g LLDPE for the casein/oil model solutions. Maximum absorption values were approximately equal to the values found in oil model solution at 1.5 g/l, suggesting that limonene, decanal and linalool (apolar flavour compounds) first dissolve in the oily phase. Only the remaining flavour compounds in the aqueous phase were available for absorption by LLDPE or interaction with pectin and casein.

Pectin can increase viscosity and interact with flavour compounds, reducing diffusion of flavour compounds from the food matrix to LLDPE.[1] In this study, the absorption of limonene was significantly ($P<0.01$) suppressed with increasing concentrations of pectin until a level of 5 mg of limonene per gram of LLDPE after 14 days was reached. For some exposure days, a significant effect of pectin and casein was found for decanal and linalool absorption, although the Duncan test results showed no clear trend.

Casein, which interacts with limonene through weak reversible hydrophobic bounds, decreased the absorption of limonene significantly ($P<0.01$) only during the initial day(s) of exposure. However, casein and decanal can interact with each other by irreversible covalent bounds, which decreased decanal absorption to almost nothing after 14 days of exposure.[15] An explanation of the increased absorption after 14 days at 40 g/l of casein could be the decrease of available binding sites due to protein-protein interactions.[16,17]

Absorption of E2MB from casein/oil or pectin/oil model solutions showed a similar zigzag pattern as was found for model solutions containing pectin or casein individually in a previous study.[1] It was concluded that the behaviour of E2MB could not be fully explained and that further investigation was required.

3.3.3 Influence of skim milk and whole milk

So far, only simple model solutions containing one or two food component had been studied with respect to their effect on the absorption of flavour compounds by LLDPE. However, real food products are usually a mixture of many food components between which flavour compounds are distributed. To compare the absorption results from the investigated model solutions with real food products, skim and whole milk were spiked with flavour compounds.

Skim and whole milk are emulsions with a complex matrix, which mainly consists of water, lactose, proteins and fat.

Figure 3.4A shows the influence of protein and fat concentration in spiked skim milk on limonene and decanal absorption by LLDPE.

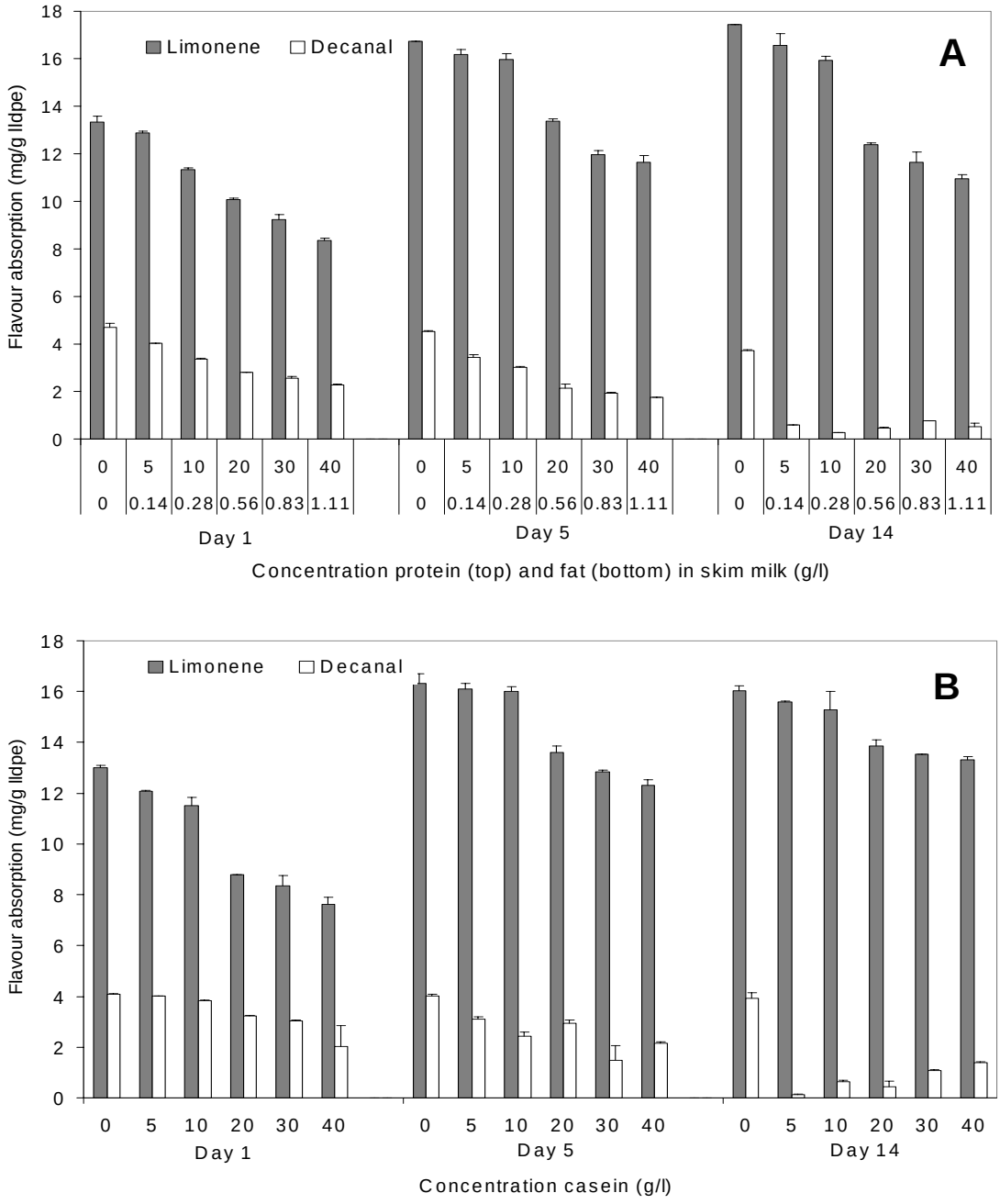

Figure 3.4 Influence of protein and fat in skim milk (A) and casein (B) on the absorption of limonene and decanal by LLDPE after 1, 5 and 14 days of exposure at 4°C.

Absorption of limonene and decanal decreased significantly with increasing concentrations of protein and fat. Regarding the amount of fat present in skim milk, the absorbed amount of limonene was higher than expected on the basis of the results from the investigated oil model

solutions. Comparison of Figure 3.4A with 3.4B (representing absorption data of previously investigated casein model solutions[1]), shows a striking similarity: not fat but the casein in skim milk is mainly responsible for the absorption decrease of limonene and decanal. An explanation could be that the small amount of fat in skim milk is bound in some way and that flavour compounds need free fat to solubilize. Widder and Fischer[2] also concluded that differences in flavour release between water and milk containing 0.3% fat were caused by interactions of flavour compounds with ingredients of milk, especially proteins, and to a lesser extent carbohydrates, salts and the small amount of fat.

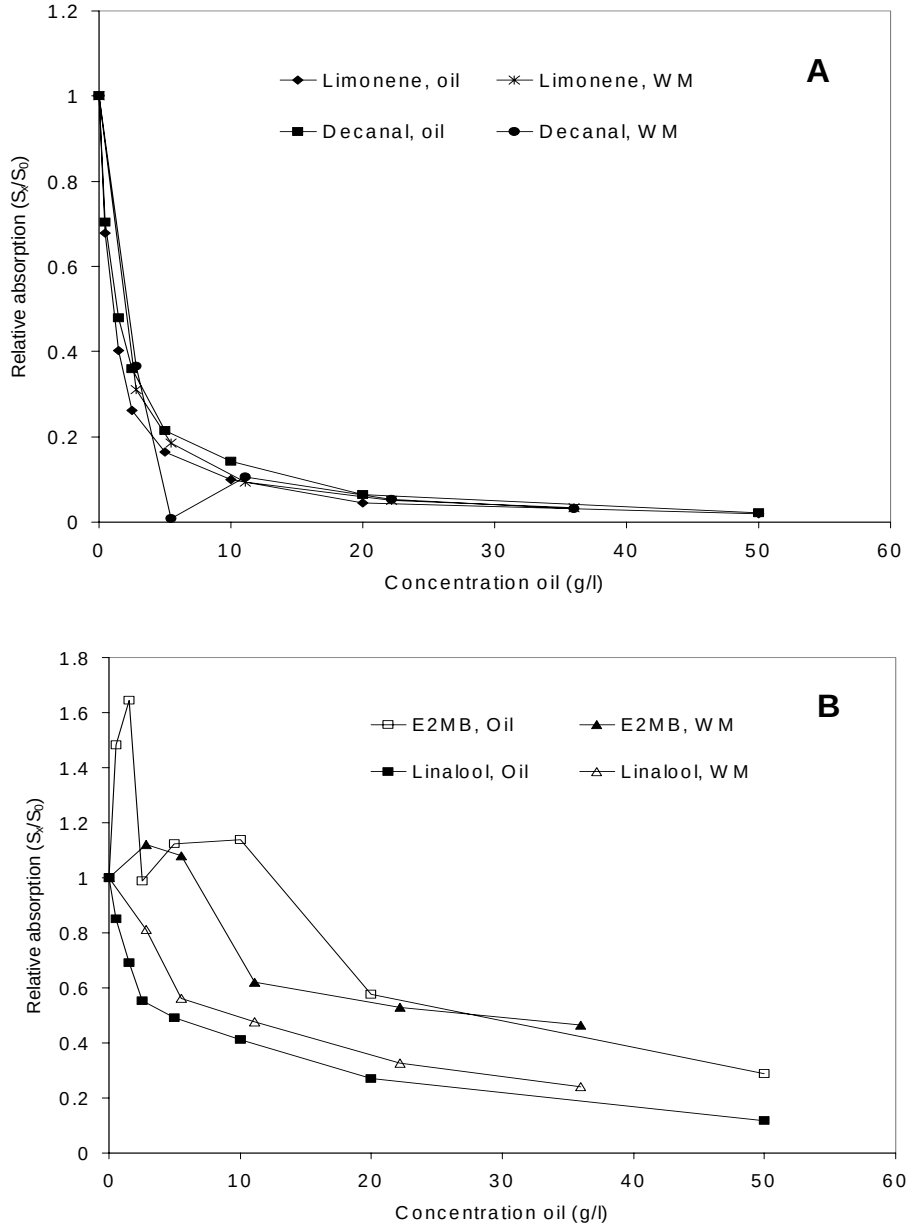

Figure 3.5 Influence of oil and fat in whole milk (WM) on the relative absorption of limonene and decanal (A) and E2MB and linalool (B) by LLDPE after 14 days of exposure at 4°C.

Investigations with whole milk, which contained a larger amount of fat than skim milk, showed that the free fat content is an important factor. After 14 days of exposure, an almost equal amount of absorbed flavour compounds and an almost similar absorption pattern were found for the whole milk samples and the oil containing model solutions (see Figure 3.5).

3.4 Conclusions

The composition of a food matrix plays a major role in the absorption of flavour compounds by LLDPE. Several studies have already revealed that flavour compounds interact with oil, carbohydrates and proteins, but the influence on flavour absorption by plastic packaging materials in different food matrices has been unclear until now. This and previous study[1] show that food components can affect the quantity of absorbed flavour compounds by LLDPE in the following order: oil or fat >> polysaccharides and proteins > disaccharides. Because of the lipophilic character of many flavour compounds, food products with a high oil/fat content will lose less flavour by absorption into LLDPE packaging than food products containing no or a small quantity of oil.

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4

Modelling the effects of the food matrix on flavour absorption

Abstract

One of the phenomena in food-packaging interactions is flavour absorption. Absorption of flavour compounds from food products into food packaging materials can result in loss of flavour compounds or an unbalance in flavour profile changing product's quality. The food matrix influences the amounts of absorbed flavour compounds, especially the presence of oil or fat determines the ability of absorption of flavour compounds from the food to the package. On the other hand the polarity of the flavour compound itself is a characteristic, which influences also the level of absorption into synthetic polymers. A model based on the effect of the polarity (log P) of flavour compounds and on their partitioning coefficients between food(matrix) and packaging material is described. The model can be used for predicting absorption of flavour compounds from foods into LLDPE. Results showed that the model fits nicely with experimental data. The model can be used when lipids in the food matrix are the main factor in determining absorption of flavour compounds. However, in a very low fat food matrix the model is not valid for compounds like aldehydes, which are able to interact strongly with proteins.

This chapter has been submitted as:

Van Willige RWG, Dekker M, Linssen JPH and Voragen AGJ, *Food Addit and Contam*

4.1 Introduction

Synthetic polymers as polyolefins, low-density polyethylene (LDPE) and polypropylene (PP), and polyesters, polyethylene terephthalate (PET) and polycarbonate (PC), are widely used for food packaging applications. Several interactions between the food and the package are responsible for the quality and shelf-life of the packaged food. These food-packaging interactions are defined as an interplay between food, packaging and the environment, which produces an effect on the food and/or package.[1]

Such interactions can be divided into three phenomena: migration, permeation and absorption. The latter one is expressed in absorption of food constituents, such as flavour compounds, into the packaging material. Several researchers reported that plastic packaging materials are able to absorb considerable amounts of flavour compounds, resulting in a loss of aroma intensity or an unbalanced flavour profile.[2-6] Also changes of the packaging material itself, as there are a delamination of multilayer packages[7,8] and increased oxygen permeation through the packaging material[9-13], cause indirect effects on the packaged foods. There are many factors that influence the level and amount of absorbed compounds in synthetic polymers, as there are the chemical composition, morphology and crystallinity of the polymer. Also the chemical composition, concentration and mixture of sorbants are important criteria. Moreover, the solubility of aroma compounds in a polymer is affected by several extrinsic factors, such as temperature, relative humidity and pH.[14] Intrinsic factors are related to the chemical composition of the packaged food itself. The presence of pulp particles in citrus fruit juices decreased absorption of flavour compounds into LDPE.[15,16] Absorption of flavour compounds into packaging materials are influenced by interactions of the flavour compounds and food components in the food matrix. Flavours may be dissolved, adsorbed, bound, entrapped, encapsulated or retarded in diffusion through the matrix by certain food components. The relative importance of each of these mechanisms varies with the properties of the flavours (functional groups, molecular size, shape, volatility, polarity, etc) and the chemical and physical properties of the components in the food.[17,18]

4.1.1 Effects of food matrix

In an extensive work we investigated the effect of food matrix on absorption of flavour compounds into linear low-density polyethylene (LLDPE).[19,20] The influence of the presence of oil, proteins and carbohydrates were investigated. The study was carried out with a mixture of 4 flavour compounds: limonene, decanal, linalool and ethyl 2-methylbutyrate. Protein systems investigated included β-lactoglobulin and casein; carbohydrate systems included pectin, carboxymethylcellulose (CMC), lactose and saccharose and lipid systems included oil in water emulsions. Also some combined models (oil/casein and oil/pectin) were investigated as well as some real foods (skim milk and whole milk). It was found that β-lactoglobulin interacted irreversibly with decanal and therefore suppressed flavour absorption substantially. Also casein was able to bind limonene and decanal, resulting in a decreased absorption of these compounds. The presence of CMC and pectin (thickening agents) slowed down diffusion of limonene and decanal from the food matrix to LLDPE, and consequently the absorption rate of limonene and to a lesser extent of decanal. Due to a 'salting out' effect lactose and saccharose increased absorption of linalool and E2MB. The presence of oil influenced absorption of the flavour compounds substantially: a relative small amount of oil (50 g/l) decreased the amount of absorbed flavour compounds with approximately 90%. Solubilization of the apolar flavour compounds into the oily phase made only the remaining flavour compounds solved in the aqueous phase available for absorption into the polymer. The oil/casein and oil/pectin models showed a similar effect. The presence of oil influenced the level of absorbed compounds to a much greater extent than proteins (e.g. casein) or carbohydrates (e.g. pectin). The findings of these model systems were confirmed with the investigated real food products: absorption results for skim milk and whole milk samples were in good agreement with the results of the investigated model systems containing the individual components. The composition of a food matrix showed to play a major role in the absorption of flavour compounds by LLDPE. The extent of flavour absorption by LLDPE is influenced by food components in the order: oil or fat >> polysaccharides and proteins > disaccharides. Knowledge of solubility and binding behaviour of flavour compounds to non-volatile food components and their partitioning behaviour between different phases (component/water, component/oil or component/oil/water on one site and water/polymer, oil/polymer or water/oil/polymer on the other site) is of main importance to estimate the rate and amount of absorption from real food products by polymers.

4.1.2 Modelling

Enormous amounts of different flavour compounds are used in foods. It is impossible to study them all. A determination of the relationship between flavour compounds and polymeric packaging materials for predicting flavour absorption would save research time for the packaging industry. Prediction of flavour absorption in relation to the packed food and the packaging material would be a valuable tool in product development. It can help the food industry in choosing packaging material or in determining product formulation. In literature little information is available on the prediction of flavour absorption. Attempts were made by using several theories. Tigani and Paik[21] used the dielectric constants of polymers and flavour compounds to predict flavour absorption. They concluded that the dielectric constant might not encompass all of the factors for an accurate prediction of absorption by polymers. Paik and Tigani[22] examined the application of Hildebrand's regular solution theory for predicting the equilibrium absorption of flavour compounds by polymer packaging materials. However, they found a poor correlation between the regular solution theory and flavour absorption values, indicating that the entropy contribution could not be assumed negligible. Paik and Writer[23] applied the Flory-Huggins equation for prediction of flavour absorption. The Flory-Huggins theory is based on the entropy contribution due to molecular size and shape differences of molecules. They showed that the Flory-Huggins equation gave much better estimations of flavour absorption than the regular solution equation. However, Flory-Huggins equation still did not adequately predict flavour absorption, but can provide a qualitative prediction of flavour absorption, which can be useful for selection and design of packaging materials. Finally, Li and Paik[24] tried to estimate flavour absorption by the UNIFAC group contribution model. The UNIquac Functional-group Activity Coefficient (UNIFAC) is based on a semi-empirical model for liquid mixtures called UNIversal QUasi-chemical ACtivity (UNIQUAC). Comparison between the experimental and calculated data indicated the UNIFAC model was much more accurate in absorption prediction than the regular solution theory and the Flory-Huggins equation.

Flavour absorption by a solid (amorphous) polymer is a meta-equilibrium state that often requires a long time to reach equilibrium. The equilibrium distribution of flavour compounds will depend on their partitioning behaviour of compounds between different phases in the system: polymeric packaging and food matrix. The properties of the package, such as polarity and crystallinity, as well as the composition of the food matrix (presence of oil, proteins, carbohydrates) are extremely important factors.

Modelling of flavour absorption could be based upon a set of equations describing these equilibrium distributions together with mass balances of the flavour compounds.
The final goal is to make predictions of flavour absorption for other food matrices and other compounds based upon their characteristics, such as polarity and molecular weight. In the future, a fitting model could be extended with the dynamics of the absorption phenomena (including mass transfer effects as a consequence of product texture, viscosity, etc.) and also for different packaging materials.

4.2 Model description

4.2.1 Partitioning equilibrium

In a food-packaging material system flavour molecules will strive for a thermodynamic equilibrium situation in which their chemical activities in all phases of the system will be equal. The time it will take to reach this equilibrium will depend on the composition of the food matrix. It can be assumed that in liquid foods this equilibrium will be reached well before consumption of the product. Experimental data of flavour absorption confirm this.[19,20]
In solid or highly viscous food products this equilibrium might take longer, in that case only the outer part of the food will be affected by the flavour absorption effect. To model the flavour absorption process it is important to take into account the most important phenomena that take place. It has been shown that for food products the effect of the aqueous and oily phase on flavour absorption is dominating. Other main food components, like proteins and carbohydrates, have a far less pronounced effect compared to oil. For a first modelling approach, therefore, the partitioning between the oily and aqueous phase and between the polymer and the aqueous phase is describing the equilibrium (equations 1 and 2):

$$K_{P/A} = \frac{C_P}{C_A} \qquad (1)$$

$$K_{O/A} = \frac{C_O}{C_A} \qquad (2)$$

in which *K* is the partitioning coefficient (-), *C* is the concentrations of the flavour compound in the different phases (all in mg/g), the indexes *P, A* and *O* refer to the polymer, aqueous and oily phase, respectively.

4.2.2 Mass balance

In a food formulation the initial amount of flavour is known. To calculate the level of flavour molecules in the packed food product we can use the mass balance, assuming no flavour is lost to the environment or chemically degraded (equation 3):

$$M_{FP} \cdot C_{FP,t=0} = M_{FP} \cdot C_{FP,t=t} + M_P \cdot C_{P,t=t} \qquad (3)$$

in which *M* is the mass (g) and *FP* refers to the food product, and t to the time. For the food product a simple mass balance holds for its aqueous and oily phase (equation 4):

$$M_{FP} = M_A + M_O \qquad (4)$$

4.2.3 Predictive modelling

With equation 1-4 the system can be described in equilibrium for oil containing food products for all flavour-packaging combinations. The equilibrium concentration in the packaging material can be calculated from equation 5, which is derived from equation 1-4:

$$C_{P,\infty} = \frac{M_{FP} \cdot C_{FP,t=0}}{M_O \cdot \frac{K_{O/A}}{K_{P/A}} + \frac{M_A}{K_{P/A}} + M_P} \qquad (5)$$

To make predictions of the extent of flavour absorption, information is required about the value of the two partition coefficients for the flavours of interest. The partitioning will depend largely on the nature of the flavour, especially on its polarity. Experimental determination of all partition coefficients is a very laborious task. Therefore, models

describing the relation of the partition coefficients with known quantitative information on the nature of the flavour molecules are valuable. In this paper we make an attempt to do this based upon the log P value of the flavours, which is a good measure of their polarity. These values are reported for many molecules and can also be calculated from their chemical structure.

4.2.4 Modelling procedure

Fitting the experimental data to the model equations has been done by minimizing the sum of squares of the relative errors between model prediction and measured data with the 'solver' routine of Microsoft Excel 97. Regression analysis was performed with the 'data analysis toolkit' of the same software package.

4.3 Results and discussion

4.3.1 Modelling the effects of oil on flavour absorption

To model the effect of edible oil on the partitioning of flavour molecules data published by [19,20] for the partitioning of limonene, decanal and linalool to LLDPE was used (the results of the more polar flavour compound ethyl 2-methylbutyrate has not been included in this study due to its very low and therefore less accurate values of absorption). The experimental data with different levels of oil (equilibrium after one day of exposure) in the system were fitted to the model equations 1-5. Figure 4.1 shows these fits.

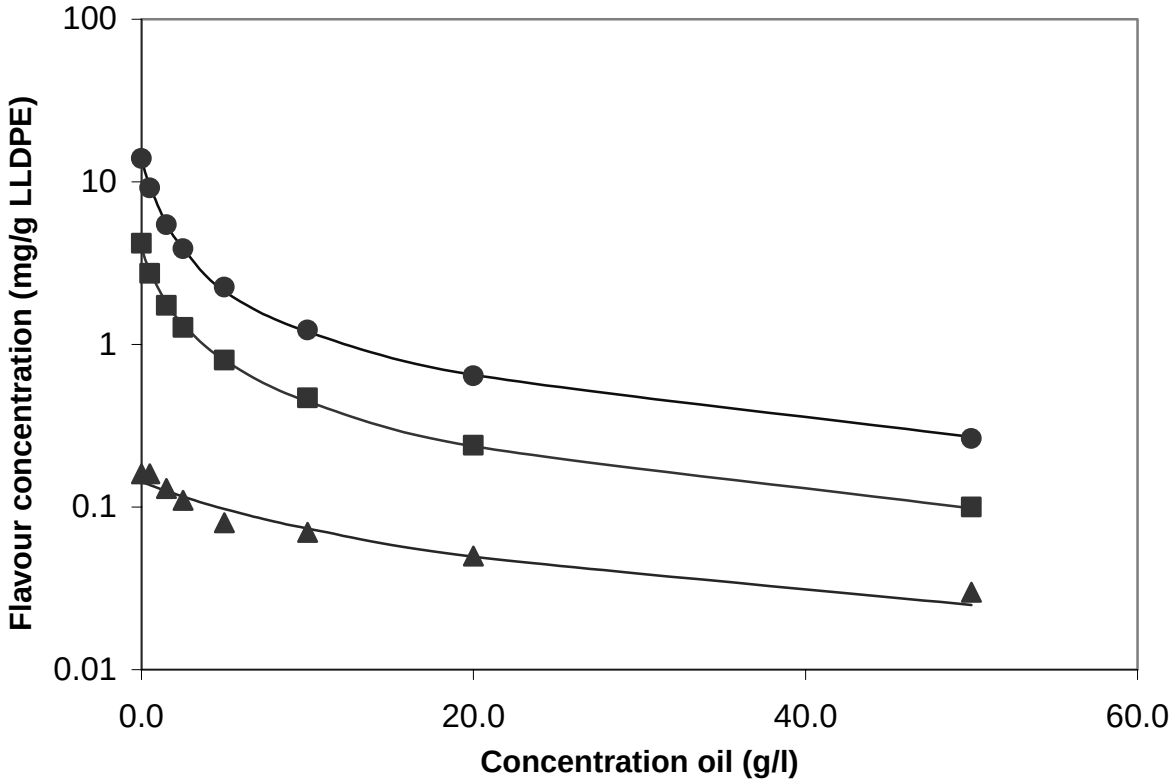

Figure 4.1 Experimental data of flavour absorption by LLDPE as function of the oil content of the oil model solutions and the model fits for limonene (●), decanal (■) and linalool (▲) after 1 day of exposure at 4°C.

A very good description of the experimental data is observed. The obtained values of the partition coefficients for the studied flavours are given in Table 4.1.

Table 4.1 Log P and partition coefficients obtained from fitting the absorption data to equations 1-5.

Flavour compound	Log P*	Log($K_{O/A}$)	Log($K_{P/A}$)
Limonene	4.58	3.09	2.27
Decanal	4.09	2.91	1.67
Linalool	3.28	1.98	0.22

* Measure of hydrophobicity, calculated with ACD/Log P v3.6 (www.acdlabs.com)

From Figure 4.1 and Table 4.1 it can be concluded that the studied flavours have a higher affinity for oil than for LLDPE. To predict the behaviour of other flavours in an oil/aqueous/polymer system we have related the obtained *K* values to the polarity of the flavour molecules. Log P represents the hydrophobicity of a flavour compound; the higher the Log P, the more hydrophobic a compound. The Log P values for limonene, decanal and

linalool are presented in Table 4.1. In Figure 4.2 the relation between log(*K*) values and the log P values of the compounds is given.

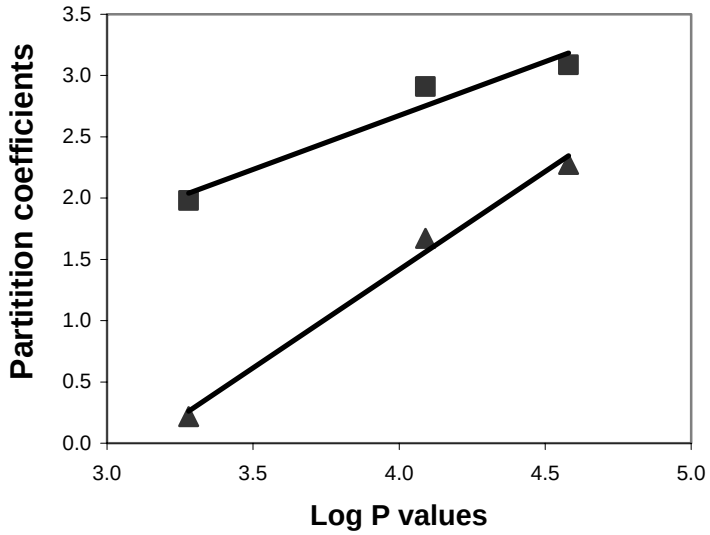

Figure 4.2 Relationship between log P values of the flavour compounds and their partition coefficients $K_{O/A}$ (■) and $K_{P/A}$ (▲) at 4°C.

Figure 4.2 shows that a linear relationship between the Log P values and the partition coefficients is obtained (R^2 is 0.95 and 0.99 for $K_{O/A}$ and $K_{P/A}$ respectively). In equation 6 and 7 the relations are given:

$$\text{Log}(K_{O/A}) = -0.85 + 0.88 \cdot \log P \qquad (6)$$

$$\text{Log}(K_{P/A}) = -5.0 + 1.60 \cdot \log P \qquad (7)$$

With equation 5 and 6 a prediction can be made of the partition coefficient of other flavour compounds, which have log P values in the range of the studied compounds (log P 3 to 5). With these values the equilibrium situation in the packed food can be predicted using equations 1-4. In this way the amount of flavour absorption is predicted, which can be used for selection of packaging concepts for giving indications for adjusting of the formulation of the product accordingly.

4.3.2 Application to foods

In most foods the main constituents of the matrix are: water, oil/fat, proteins and carbohydrates. It was shown by Van Willige *et al.*[19] that the amount of oil/fat present in the food is the main factor affecting flavour absorption. The phenomenon of binding of flavour molecules to proteins can also play a role, especially in (very) low fat systems. Van Willige *et al.*[19] presented data of flavour absorption in a LLDPE/milk (skim milk and whole milk) system spiked with the flavour compounds, limonene, decanal and linalool. We have compared these data with predicted data using the modelling approach as described in the previous section (Table 4.2). By doing so we ignore the possibility of binding of flavours to proteins or carbohydrates present in the products. Figure 4.3 shows a plot of these data.

Table 4.2 Comparison between predicted data and measured data for flavour absorption into LLDPE from skim and whole milk after 1, 5 and 14 days of exposure at 4°C.

	Flavour absorption (mg/g LLDPE)							
	Skim milk (0.11% fat)				Whole milk (3.6% fat)			
Flavour compound	Predicted	Measured day 1	Measured day 5	Measured day 14	Predicted	Measured day 1	Measured day 5	Measured day 14
Limonene	6.50	8.34	11.63	10.96	0.36	0.41	0.46	0.53
Decanal	2.11	2.29	1.76	0.52	0.14	0.13	0.31	0.12
Linalool	0.13	0.20	0.20	0.17	0.03	0.00	0.00	0.05

As can be seen from Table 4.2 and Figure 4.3 our model description is quite valid for short-term exposure (1 day). For these experiments the predictions match the measured values quite well both for skim and whole milk. For prolonged exposure (14 days) there is a significant deviation of the measured absorption of decanal in skim milk with the predicted value (minus 75%). This should be explained by a binding of decanal to proteins (most likely casein), which is having a substantial effect on the free concentration of decanal in the aqueous phase and thus on the amount of decanal available for absorption into LLDPE.[19] The experimental results for the absorption of flavour compounds from milk products and the comparison with the partitioning model show that a very good prediction is obtained in most situations. However, in special cases deviations may occur in (very) low fat products containing flavour compounds that have a high affinity for binding to proteins, as was observed for decanal in

skim milk. Predictive models for flavour absorption from (very) low fat products will require more knowledge of the factors that affect binding of flavour compounds to proteins and to lesser extent to carbohydrates. The modelling of binding of flavour compounds to proteins

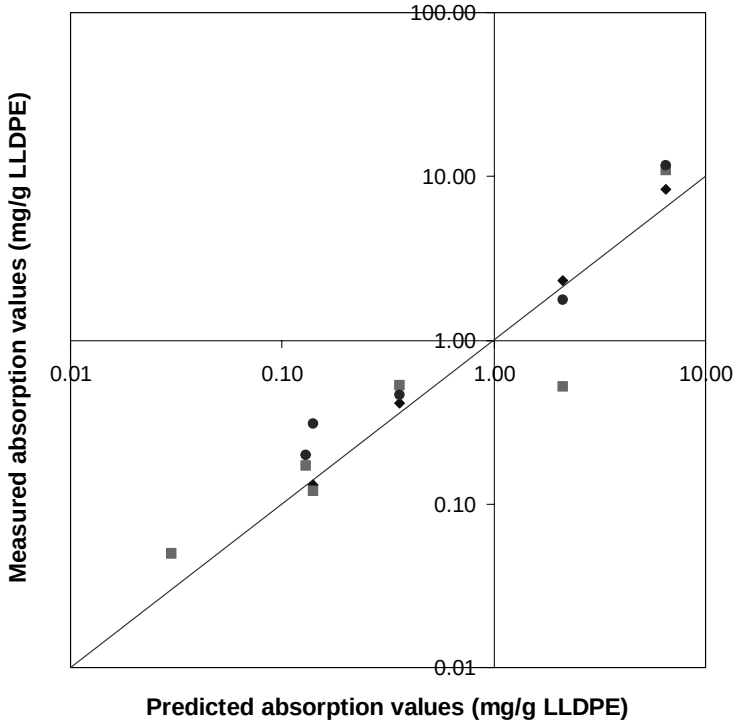

Figure 4.3 Comparison between predicted and measured absorption values for skim and whole milk after 1 day (♦), 5 days (●) and 14 days (■) of exposure at 4°C.

will be a more complicated task since the interactions between these molecules will depend on the particular flavour compound and protein combination.

4.4 Conclusion

The modelling of the absorption of flavour molecules into LLDPE based on the partitioning behaviour between the different phases in the systems enables the prediction of this phenomenon based on the polarity of the flavour compounds involved. This can limit the amount of work that would be required for experimentally determination of the amount of absorption in product development. The approach has been shown to be valid also in real food products like milk products. Only in (very) low oil/fat products the experimental data deviate from the predicted values due to the interactions of particular flavour compounds

(like aldehydes) with proteins. Future research could focus on the extension of this modelling approach for other polymer packaging materials and other conditions.

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5

Influence of storage time and temperature on absorption of flavour compounds from solutions by plastic packaging materials

Abstract

Linear low-density polyethylene (LLDPE), oriented polypropylene (PP), polycarbonate (PC), polyethylene terephthalate (PET film and PET bottle) and polyethylene naphthalate (PEN) were stored in a model solution containing 10 flavour compounds at 4, 20 and 40°C and flavour absorption by the plastic materials was followed in time. The absorption rate and/or total amount absorbed increased considerably with temperature from 4 to 40°C. Depending on storage temperature, total flavour absorption by the polyolefins (LLDPE and PP) was 3 to 2400 times higher than by the polyesters (PC, PET and PEN). From the point of view of flavour absorption, polyesters are preferred over the polyolefins as packaging material.

This chapter has been accepted as:

Van Willige RWG, Schoolmeester DN, Van Ooij AN, Linssen JPH and Voragen AGJ, *J Food Sci.*

5.1 Introduction

Packaging materials are used extensively to protect and preserve food products in storage and distribution environments. Food products may undergo loss of quality due to failure of the package and/or product-package interactions. Product-package interactions can be defined as an interplay between product, package and the environment, which produces an effect on the product and/or package.[1] Already some decades ago, pioneering research about interactions between flavour compounds and polymer films was reported.[2-4] As plastic packaging is more and more used for direct contact with foods, absorption of flavour compounds is becoming an important product-package interaction aspect. Flavour absorption may alter the aroma and taste of a product[5] or change the mechanical properties of polymers, such as tensile strength[6] and permeability.[7] The extent of flavour absorption is influenced by the properties of the polymer and the flavour molecules, and also by external conditions. The chemical composition, chain stiffness, morphology, polarity and crystallinity of the polymer, as well as the chemical composition, concentration, polarity of the flavour compounds, and the presence of other chemical compounds are important factors. External factors such as storage duration, relative humidity, temperature and the presence of other food components can also affect solubility of aroma compounds in a polymer.[8-13]

The most widely used polymers for food-packaging applications are the polyolefins, i.e. polyethylene (PE) and polypropylene (PP). Polyolefins are used as an interior lining in box-type containers for beverages because of their good heat sealability and excellent moisture resistance. However, low-molecular-weight compounds, especially apolar compounds (such as most flavour substances) are readily absorbed.[14] The use of plastic bottles, especially polyethylene terephthalate (PET) bottles for carbonated beverages, is increasing steadily. PET is a relatively good barrier against permeation of gases and flavour compounds, due to the biaxial orientation of the molecules.[15] As a relatively new member of the polyester family polyethylene naphthalate (PEN) has excellent performance characteristics due to its high glass transition temperature (Tg). In comparison to PET, PEN provides approximately 5 times the barrier for carbon dioxide, oxygen or water vapour transmission. PEN also provides better performance at high temperatures than PET, allowing hot-fill, rewash and reuse. However, the cost of PEN is about 3 to 4 times that of PET.[16] PEN would likely be used for niche markets such as beer[17], where the superior barrier properties of PEN may win out over other choices despite PEN's higher cost. A few years ago a reusable polycarbonate (PC)

bottle was successfully introduced by the Dutch dairy industry. These bottles take advantage of their toughness (breakage resistance) and transparency (visibility of contents). The fact that PC is much lighter than glass provides fuel savings in rolling and carrying, as well as productivity improvements, since several bottles can be handled at once. The disadvantages of PC are its high cost and its poor gas barrier properties.[18] Several investigations have shown that PE and PP can absorb considerable amounts of flavour compounds. However, less information is available in literature about the amount of flavour absorption by PET, PEN and PC. Our objective was to investigate the influence of temperature and storage time on the amount of flavour absorption by LLDPE, PP, PC, PET and PEN.

5.2 Materials and methods

5.2.1 Materials

Polymer packaging films used were linear low-density polyethylene (LLDPE; Dowlex 5056E; Dow Benelux NV, Terneuzen, The Netherlands), oriented polypropylene (PP; Bicor® MB200; Mobil Plastics Europe, Kerkrade, The Netherlands), polycarbonate (PC; Lexan® 8B35; General Electric Plastics, Bergen op Zoom, The Netherlands), polyethylene terephthalate (PET; Melinex® 800; DuPont Teijin Films, Luxembourg, Luxembourg), polyethylene naphthalate (PEN; Kaladex® 1000; DuPont Polyester Films, Wilton, Middlesbrough, UK). Oriented PET bottles, supplied by Schmalbach-Lubeca (Bierne, France), were also studied. Characteristics of the polymers used in this study are listed in Table 5.1. Decanal, hexanal, 2-nonanone, octanol and (R)-carvone were purchased from Merck (Darmstadt, Germany), hexyl acetate (HA) and myrcene from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA), linalool and ethyl 2-methylbutyrate (E2MB) from Acros Organics (Fisher Scientific UK Ltd, Loughborough, UK) and (+)-limonene from Sigma Chemical Co. (St. Louis, MO, USA). The aroma compounds were selected based on differences in functional groups, polarity and absorption affinity by the different polymers. Characteristics of the flavour compounds are listed in Table 5.2. Log P represents the hydrophobicity of a flavour compound; a higher Log P means a more hydrophobic compound.

Table 5.1 Characteristics of the polymers used in this study.[a]

Polymer	Polarity	Tg [b] (°C)	Crystallinity (%)	Thickness (μm)	Density (g/cm^3)
LLDPE film	Apolar	-75	45	50	0.921
PP film	Apolar	-5 to 0	80	30	0.916
PC film	Polar	+145	0	75	1.20
PET film	Polar	+78	45	50	1.40
PET bottle	Polar	+78	22 to 25	300	1.37
PEN film	Polar	+120	45	75	1.36

[a] Specifications from manufacturers
[b] Glass transition temperature

Table 5.2 Characteristics of the flavour compounds used in the model solutions.

Flavour compound	bp (°C)	Log P[b]	Solubility[c] (g/l)	Density (g/ml)	MW (g/mol)
Linalool	195	3.28	0.11	0.87	154.3
Octanol	177	3.00	0.21	0.82	130.2
Hexanal	130	1.78	2.89	0.81	100.2
Decanal	208	4.09	0.012	0.83	156.3
E2MB[a]	133	2.12	2.47	0.87	130.1
HA[a]	168	2.83	0.37	0.88	144.2
(R)-Carvone	230	2.23	2.11	0.96	150.2
2-Nonanone	192	3.30	0.21	0.82	142.1
(+)-Limonene	178	4.58	0.0027	0.84	136.1
Myrcene	167	4.58	0.0026	0.80	136.1

[a] E2MB = ethyl 2-methylbutyrate; HA = hexyl acetate
[b] Measure of hydrophobicity, calculated with ACD/Log P v3.6 using the ACD/I-Lab service[19]
[c] Solubility at 25ºC in water, calculated with ACD/Aqueous Solubility v4.0 using the ACD/I-Lab service[19]

5.2.2 Preparation of model flavour solutions

At t=0 mixtures of the 10 flavour compounds were freshly prepared by dissolving the flavour compounds (each 100 µl/l) in 6 g/l aqueous Tween 80 (pH = 4.2 ± 0.2). Tween 80 from Merck was used as an emulsifier, to disperse the flavour compounds in the aqueous phase. Sodium azide from Merck was added at a concentration of 0.2 g/l to prevent microbial growth. Flavour compounds were added using a micropipet (Micropipette) equipped with a glass capillary tube (Socorex, Lausanne, Switzerland). An Ultra Turrax T25 (IKA-Labortechnik, Staufen, Germany) was used for homogenisation for 2 min at 9500 rpm.

5.2.3 Exposure conditions

Strips of LLDPE (1.5 x 2.0 cm), PP (1.5 x 2.0 cm), PC (1.5 x 10.0 cm), PET (1.5 x 20.0 cm), PEN (1.5 x 20.0 cm) and PET bottle (1.0 x 10.0 cm, cut from the middle part of the bottle) were individually placed into 15-ml Teflon screw-cap vials (Supelco, Bellefonte, PA, USA) and fully immersed in the model solution (15 ml). Due to the low absorption values of PC, PET and PEN it was necessary to increase the strip size of these polymers. Samples and model solution without strips (control) were stored in the dark at 4, 20 and 40°C. LLDPE and PP strips were in contact with the model solution for 1, 3, 5, 7 h and 1, 7 and 14 days. Due to their low absorption rate PC, PEN and PET were exposed to the model solution for 7, 14, 21 and 28 days. In preliminary experiments no significant edge absorption effect was found for the investigated flavour compounds. Strips and model solutions were analysed using Large Volume Injection Gas Chromatography (LVI-GC) and static headspace GC, respectively.

5.2.4 LVI-GC 'in-vial' extraction of the polymer strips

After exposure the strips were removed from the model solution, rinsed with ethanol for 10 s, and thoroughly wiped with paper tissue to remove excess of the model solution. The strips were cut in small pieces and immediately placed into 10-ml vials containing 5 ml n-hexane (Enviroscan®; Labscan, Dublin, Ireland) or 5 ml of a 2:1 mixture of n-pentane: dichloromethane (Labscan). The choice of extraction solvent was based on extraction efficiency and extraction time. The vials were tightly closed with a Teflon/silicone seal and an aluminium crimp cap. In-vial extraction was carried out for 60 min in an ultrasonic bath (Ultrawave, Cardiff, UK). Longer ultrasonic treatment did not achieve better extraction. Recovery values (polymer + solution) of all flavour compounds were in the range of 95-102% after 1 day of exposure. GC analysis was performed using a LVI-GC system (Ultra Trace™; Interscience, Breda, The Netherlands) as described in a previous paper.[12] The LVI-GC conditions and extraction solvents used, are listed in Table 5.3.

Table 5.3 Large-volume injection GC conditions.

Extraction solvent	Hexane		Pentane : Dichloromethane (2:1)
Conditions	LLDPE, PP, PC	PEN	PET
Injection volume	30 µL	200 µL	200 µL
Injection speed	5 µL/s	2 µL/s	3 µL/s
Sec. cooling time	10 s	30 s	5 s
SVE delay time	10 s	30 s	5 s
SVE temperature	200°C	200°C	200°C
FID temperature	290°C	290°C	290°C
Oven programme	50°C (10') => 5°C/min =>190°C => 30°C/min => 280°C (5')		40°C (10') => 5°C/min => 190°C => 30°C/min => 280°C (5')

Helium was used as carrier gas at a constant flow of 2.3 ml/min. Calibration curves (r^2>0.997) were established for each component with the external standard method. A relative standard deviation (RSD) of less than 10% was found between triplicate determinations. To enable a direct comparison of results between the polymer samples, having a difference in thickness and exposed area, concentrations of flavour compounds found in the extracts were converted to surface-related values (mg/dm^2 or µg/dm^2) taking double side exposure of the strips into account.

5.2.5 Static headspace GC extraction of the model solutions

Besides absorption of flavour compounds by packaging materials flavour changes in the model solution can also be induced by other factors, for example, degradation of flavour compounds due to storage or higher temperatures. Because such reactions can influence the absorption behaviour it was necessary to determine the remaining quantity of flavour compounds in the model solutions. The concentration of flavour compounds in 100 µL of model solution was calculated from the partition coefficients (headspace/model solution) of each flavour compound which were determined at t=0 and after each exposure period using static headspace GC. Calculation method, equipment and GC conditions used have been described in a previous paper.[12]

5.3 Results and Discussion

5.3.1 Flavour absorption by LLDPE and PP

The values of the 10 flavour compounds absorbed by LLDPE and PP film during 14 days of storage at 4, 20 and 40°C are summarized in Figures 5.1 and 5.2. Flavour absorption by LLDPE and PP reached equilibrium on day 7 for most of the flavour compounds. LLDPE and PP easily absorbed limonene (2.37 and 1.77 mg/dm^2) and myrcene (1.82 and 1.78 mg/dm^2), followed by decanal, hexyl acetate and nonanone. E2MB, carvone, linalool, octanol and hexanal were absorbed in the smallest quantities. The absorption behaviour of different classes of flavour compounds depends to a great extent on their polarity.

Different plastic materials have different polarities; hence their affinities toward flavour compounds may differ from each other.[20] In the present study, observed differences in absorption by LLDPE and PP (both apolar) follow the inverse order of polarity of the flavour compounds (Table 5.1), according the rule that 'like dissolves like'. A similar trend was reported for PP by Lebossé *et al.*[21] An exception to this rule were the 2 alcohols (linalool and octanol), which were absorbed in smaller quantities than the more polar flavour compounds E2MB, HA and carvone. This was probably due to structural differences or to the capability of alcohols to form hydrogen bonds in the aqueous phase. The effect of polarity was also observed by comparing the absorption behaviour of limonene and carvone. These flavour molecules have similar structures, but limonene is an apolar terpene while carvone is a polar oxygenated terpene. Due to this difference in polarity limonene was absorbed in larger quantities than carvone.

Absorption of the aldehydes was related to their structure, that is, the length of the carbon chain. The shorter chain C-6 aldehyde hexanal was absorbed less than the C-10 aldehyde decanal. With increasing carbon chain length the polarity decreases and, consequently, the absorption increases. Shimoda *et al.*[22] reported that in a homologous series of saturated aldehydes (hexanal through dodecanal), the partition coefficient (plastic/solution), increased with the molecular weight indicating an increase in absorption. The difference in absorption behaviour of the esters E2MB and hexyl acetate also suggests an influence of the carbon chain length and thus polarity. Strandburg *et al.*[23] showed that this was the case for absorption of linear esters by different polymer films.

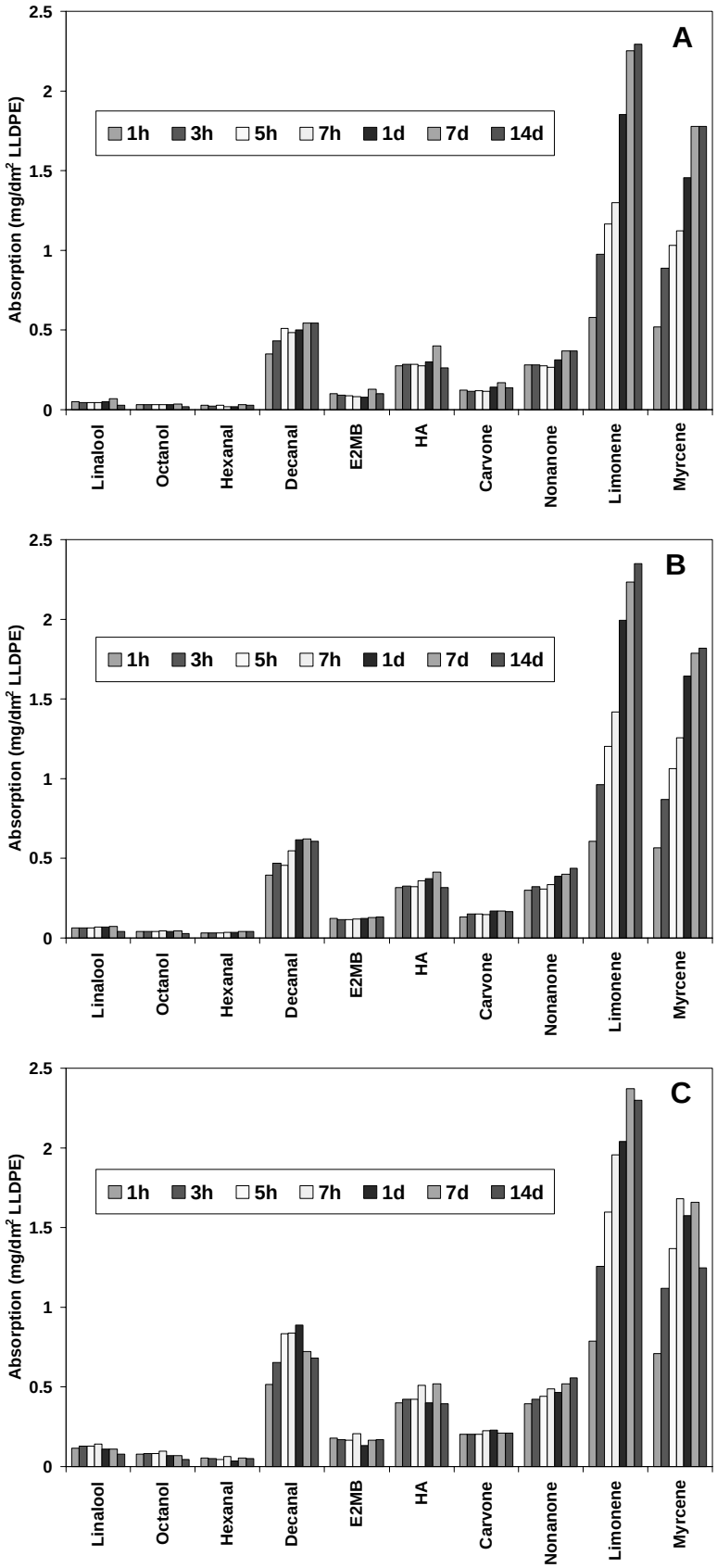

Figure 5.1 Absorption of flavour compounds by LLDPE (mg/dm^2) after different storage times at (A) 4°C, (B) 20°C and (C) 40°C.

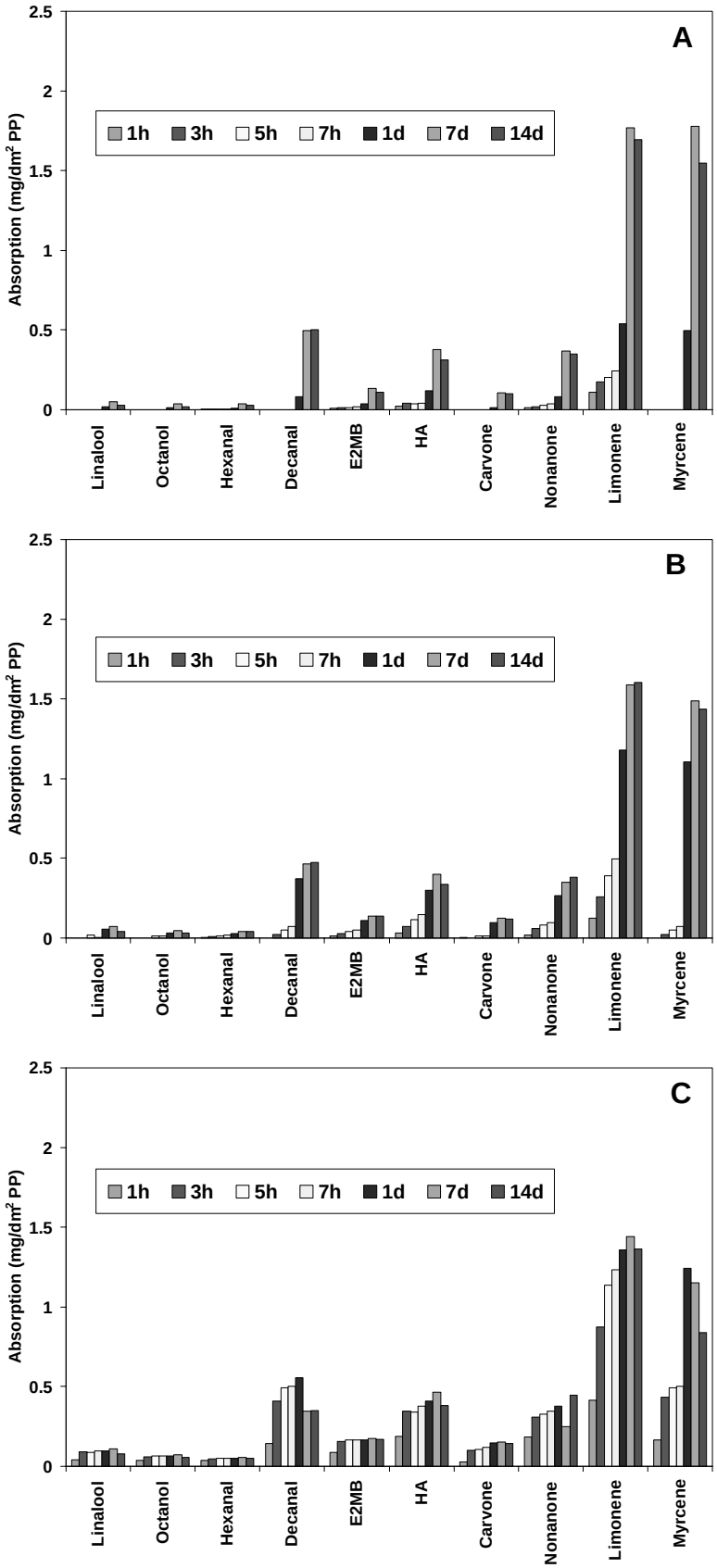

Figure 5.2 Absorption of flavour compounds by PP (mg/dm^2) after different storage times at (A) 4°C, (B) 20°C and (C) 40°C.

5.3.2 Flavour absorption by PC, PET and PEN

Figures 5.3 – 5.6 show the absorption values of the flavour compounds by PC, PET (film and bottle) and PEN during 28 days of storage at the 3 test temperatures. These 4 polymer samples showed a different absorption behaviour for the 10 flavour compounds compared with LLDPE and PP. Hexyl acetate and nonanone were the most readily absorbed, followed by decanal and carvone. Due to structural differences and the more polar character of PC, PET and PEN the apolar terpenes limonene and myrcene were absorbed in smaller quantities than the above-mentioned flavour compounds. For most of the flavour compounds absorption continued during the entire period of storage. The thickness of the polymers and/or the slow absorption rate might explain why a stable value was not reached as rapidly as was found for LLDPE and PP. Nielsen[24] showed that the absorption equilibrium of limonene and myrcene by PET was not achieved even after 12 weeks of storage at 25°C. Major differences were also found between amounts of flavour compounds absorbed by the different polymers. Depending on storage temperature, total flavour absorption by LLDPE and PP was 3 to 2400 times higher than by the polymers PC, PET and PEN. This difference was considered attributable to the difference in Tg between the materials (Table 5.1). LLDPE and PP were in the rubbery state at the investigated temperatures consequently having high diffusion coefficients for flavour compounds. The time to reach steady-state is established quickly in such structures. The glass transition temperatures of PC, PET and PEN are much higher than the test temperatures, meaning that these polymers were in the glassy state. These glassy polymers have very low diffusion coefficients for flavour compounds.[25-27] Yamada *et al.*[27] concluded from this result that absorption of flavour compounds could be reduced if the glass transition temperature of the polymer is much higher than the storage temperature. Difference in glass transition temperature might also explain the difference in absorbed flavour quantities between PET and PEN. Although the Tg of PC was much higher than the Tg of PET and PEN, absorption of flavour compounds by PC was much higher than by PET and PEN. This was attributed to the lack of crystalline regions in PC, which is a totally amorphous polymer. Letinski and Halek[28] showed that amorphous regions in a polymer have a higher affinity for flavour compounds than crystalline regions. PC will, therefore, exhibit more flavour absorption than the semi-crystalline PET and PEN.

The difference in thickness between the PET bottle and PET film samples was probably responsible for the larger flavour absorption values found by the PET bottle strips.

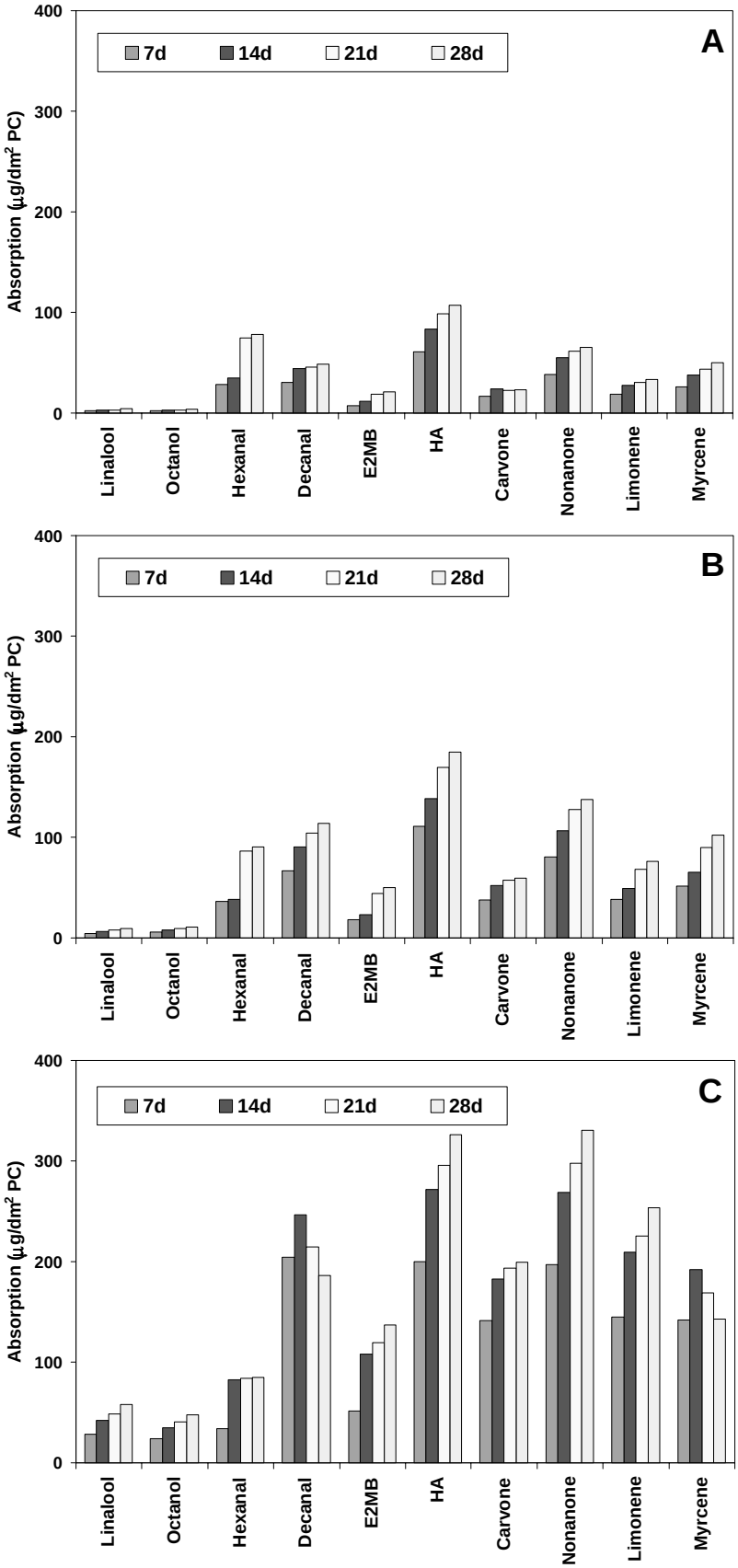

Figure 5.3 Absorption of flavour compounds by PC (µg/dm^2) after different storage times at (A) 4°C, (B) 20°C and (C) 40°C.

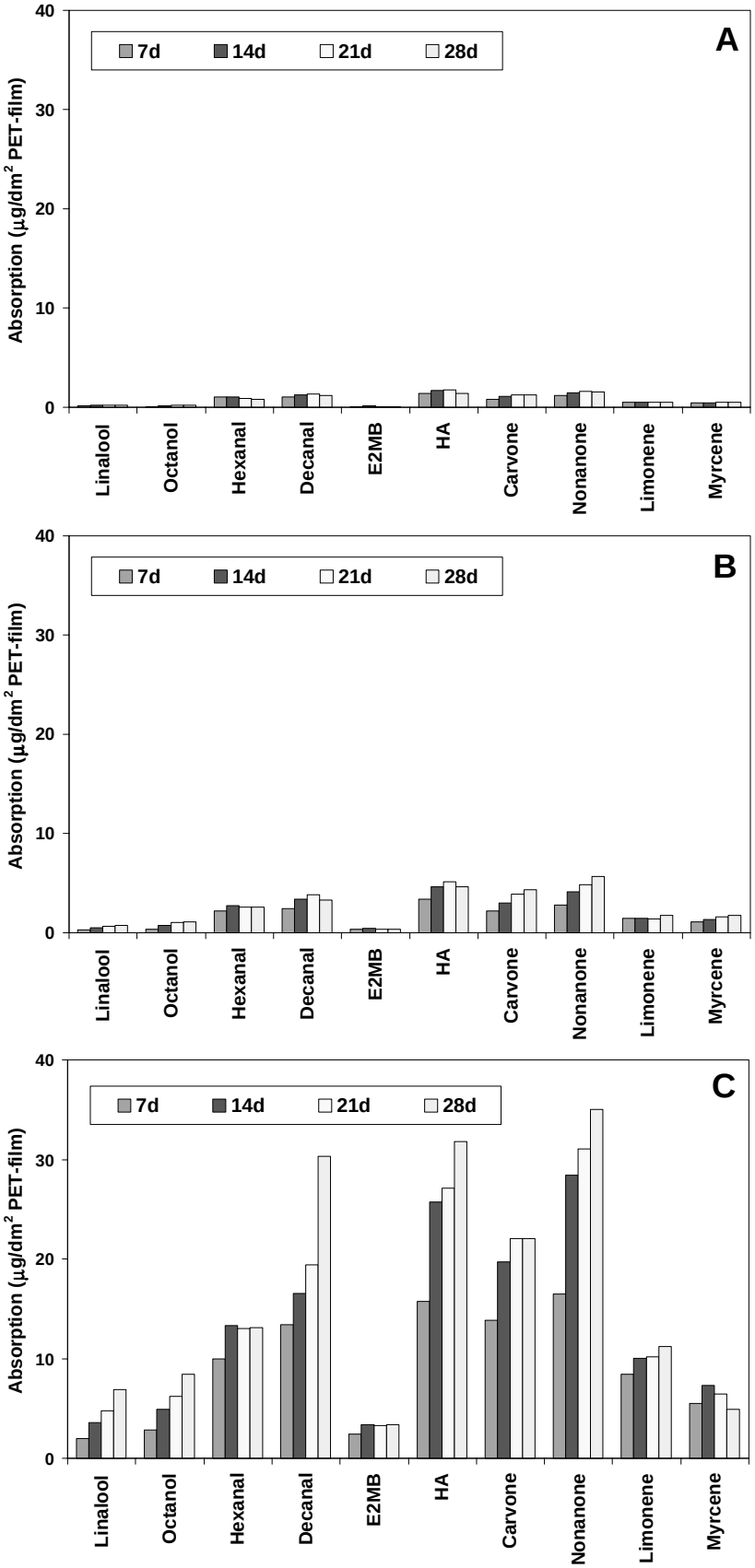

Figure 5.4 Absorption of flavour compounds by PET-film (µg/dm^2) after different storage times at (A) 4°C, (B) 20°C and (C) 40°C.

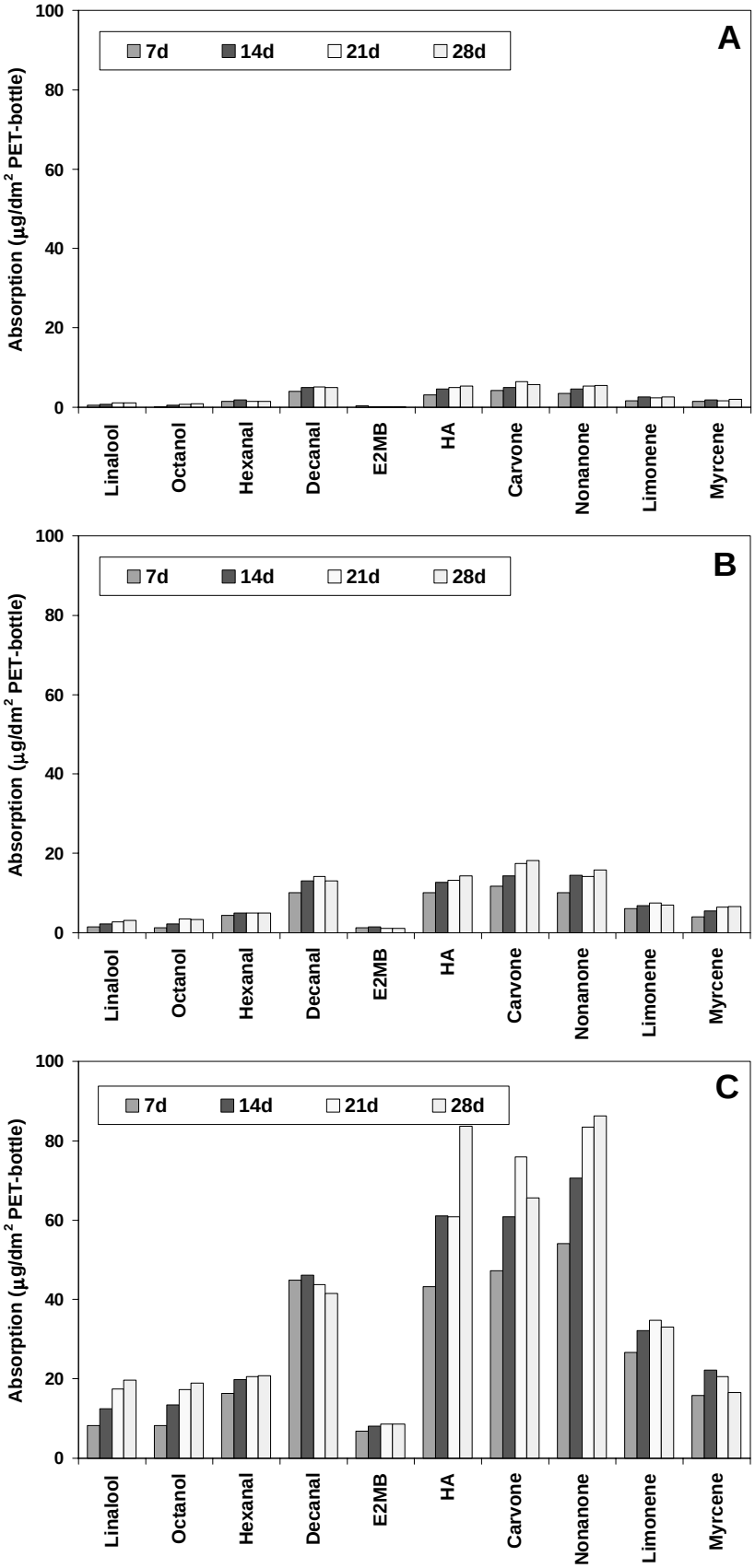

Figure 5.5 Absorption of flavour compounds by PET-bottle (µg/dm^2) after different storage times at (A) 4°C, (B) 20°C and (C) 40°C.

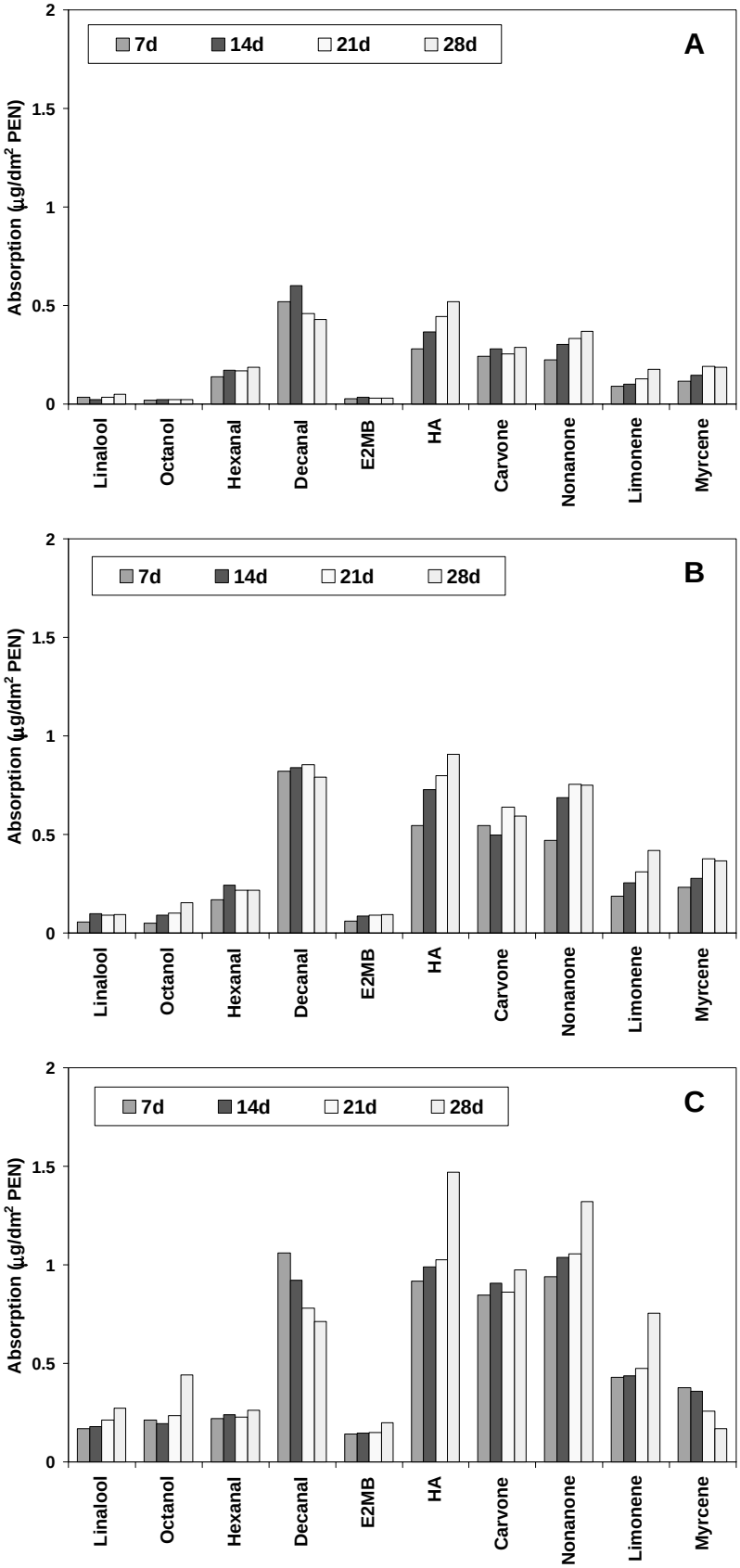

Figure 5.6 Absorption of flavour compounds by PEN (µg/dm^2) after different storage times at (A) 4°C, (B) 20°C and (C) 40°C.

5.3.3 Influence of storage temperature on flavour absorption

All investigated polymers showed an increased absorption rate at higher storage temperatures. Absorption equilibrium of LLDPE and PP was reached more quickly due to a more rapid diffusion process at higher temperatures. Also, Nielsen *et al.*[11] reported that temperature affected the absorption of flavour compounds by LDPE significantly. They also found a higher flavour absorption level; approximately twice as much was absorbed at 75°C compared with 5°C. They suggested that this increase was due to the greater mobility of the molecules, or due to swelling of the polymer at higher temperatures creating more space for solvation of the flavour molecules. In the present study a higher flavour absorption level and a higher flavour absorption rate with increasing storage temperatures was only found for PC, PET and PEN. A combination of a faster diffusion process and a higher equilibrium constant (polymer/solution) at the higher storage temperatures resulted in a higher amount of flavour absorption.Van Lune *et al.*[15] showed that absorption of toluene and methanol by PET and PEN bottles increased with increasing temperature, which was partly due to an increase in the diffusion coefficient of the contaminants with increasing temperature. They also suggested that the crystallinity of PET decreased and that the free volume increased at higher temperatures, resulting in molecules being absorbed more easily. In another study, Tawfik *et al.*[6] reported that PET stored for 15 days at 37°C in a model solution containing 320 ppm limonene absorbed 7 times more limonene than when stored at 5°C, but only 4 times more after 45 days. They concluded that the diffusion process was temperature-dependent, as could be expected from the slower rate at a lower temperature.

With the exception of decanal absorption by PET film, absorbed quantities of decanal and myrcene decreased during prolonged storage after reaching a maximum absorption level at 40°C (Figure 5.1C-5.6C). Apparently, decanal and myrcene desorbed from the polymers to the model solution. Figure 5.7 shows the influence of storage time and temperature on the concentration of decanal and myrcene in a model solution without a polymer sample.

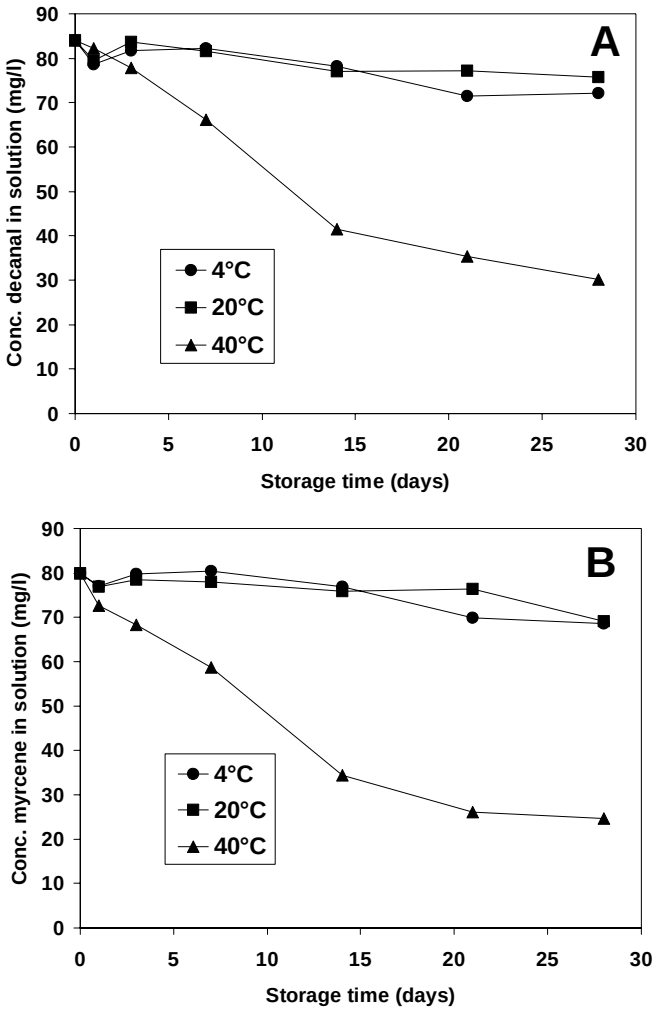

Figure 5.7 Influence of storage time and temperature on the concentration of decanal (A) and myrcene (B) in a Tween 80 model solution without polymer sample.

At 40°C the concentration of decanal and myrcene in the model solution (determined with static headspace analysis) decreased with 64% and 71%, respectively, due to degradation of decanal and myrcene. This degradation process caused a desorption of decanal and myrcene from the polymer samples in order to re-establish the equilibrium between polymer and solution. With increasing storage time and temperature degradation of aldehydes (octanal, decanal and citral) was also observed in orange juice by other researchers[29,30], however no explanation for this process was given. All the other investigated flavour compounds were quite stable in the model solution at all 3 storage temperatures.

Table 5.4 shows the influence of storage temperature on the total amount of flavour absorption by all investigated polymer samples after 14 or 28 days of storage. An increase in temperature had no remarkable effect on flavour absorption by LLDPE. At 40°C a slight decrease of the total flavour absorption by PP was measured due to the degradation of mainly

decanal and myrcene. A more pronounced effect of storage temperature on flavour absorption was found for the glassy polymers, PC, PET and PEN. After 28 days of storage at 40°C total flavour absorption by PET film and PET bottle increased by a factor 21.3 and 13.3, respectively, compared to storage at 4°C. Total flavour absorption by PC and PEN increased by a factor 4.1 and 2.9, respectively, when increasing the storage temperature from 4 to 40°C. Temperature seemed to have a more pronounced effect on flavour absorption by PET than on flavour absorption by PC and PEN. With the increase of temperature, the difference with the Tg of PET became smaller and smaller, which probably caused a relaxation (that is, an increased free volume) of the polymer network. PC and PEN, having a higher Tg than PET, were obviously less affected.

Table 5.4 Temperature effect on the total amount of flavour absorption by different polymers after 14 or 28 days of storage at 4, 20 and 40 °C.

Polymer	Temperature (°C)	Total absorption at day 14 (mg/dm^2)	Temperature effect		
			4 - 20°C	20 - 40°C	4 - 40°C
LLDPE film	4	5.6	1.1		
	20	5.9		1.0	
	40	5.7			1.0
PP film	4	4.7	1.0		
	20	4.6		0.8	
	40	3.9			0.8
Polymer	Temperature (°C)	Total absorption at day 28 (µg/dm^2)	Temperature effect		
			4 - 20°C	20 - 40°C	4 - 40°C
PC film	4	434.7	1.9		
	20	834.5		2.1	
	40	1765.4			4.1
PET film	4	7.8	3.4		
	20	26.3		6.3	
	40	167.2			21.3
PET bottle	4	29.6	3.0		
	20	87.6		4.5	
	40	394.8			13.3
PEN film	4	2.3	1.9		
	20	4.4		1.5	
	40	6.6			2.9

5.4 Conclusions

All packaging materials show a certain absorption capacity for flavour compounds. Rate and quantity of flavour absorption are related to differences in polymer characteristics (such as polarity, Tg and crystallinity) and to the structure and polarity of the different flavour compounds. Absorption of flavour compounds by PC, PET and PEN is much less than by the polyolefins LLDPE and PP. From the point of view of flavour absorption and loss of flavour compounds, PC, PET and PEN should be preferred over LLDPE and PP. On the other hand, storage temperature does not seem to influence the total amount of flavour absorption by the rubbery polymers LLDPE and PP, while temperature raises do seem to affect flavour absorption rate and quantity by the glassy polymers PC, PET and PEN.

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6

Influence of flavour absorption on oxygen permeation through LDPE, PP, PC and PET plastics food packaging materials

Abstract

The effect of flavour absorption on the oxygen permeability of low-density polyethylene (LDPE), polypropylene (PP), polycarbonate (PC) and polyethylene terephthalate (PET) was studied using an isostatic continuous flow system. Polymer samples were exposed to a model solution containing limonene, hexyl acetate, nonanone and decanal at 40°C. After exposure, one part of each sample was analysed for absorbed flavour compounds using a Large Volume Injection GC Ultrasonic 'in vial' extraction method, and from the other part the oxygen permeability was measured in a permeation cell at 25°C. After 8 hours of exposure, LDPE and PP samples showed a significant linear (R^2=0.82 and R^2=0.99) increase of the oxygen permeability of 21% and 130%, respectively. Owing to swelling of the polymer samples resulting from flavour absorption, the structure of the polymeric network changed (i.e. opened) and consequently increased oxygen permeability. The oxygen permeability of exposed PC showed a significant linear (R^2=0.78) decrease of 11% after 21 days. PC obviously did not swell like LDPE or PP. Therefore it was suggested that absorbed flavour compounds occupied or blocked 'micro-cavities' through which normally oxygen is transported. Absorption of flavour compounds by PET did not affect the oxygen permeability of PET significantly.

This chapter has been published as:
Van Willige RWG, Linssen JPH, Meinders MBJ, Van der Stege HJ and Voragen AGJ, *Food Addit and Contam* **19:**303-313 (2002).

6.1 Introduction

An important requirement in selecting food-packaging systems is the barrier properties of the packaging material. Barrier properties include permeability of gases (such as O_2, CO_2, N_2 and ethylene), water vapour, aroma compounds and light. These are vital factors for maintaining the quality of foods. A good barrier to moisture and oxygen keeps a product crisp and fresh, and reduces oxidation of food constituents. Plastics are widely used for food packaging due to their flexibility, variability in size and shape, thermal stability, and barrier properties. Polyethylene (PE) and polypropylene (PP) have been used for many years because of their good heat sealability, low costs and low water vapour permeability. However, poor gas permeability makes laminating of PE with aluminium foil and paper necessary. During the last decades, polyethylene terephthalate (PET) and, to a lesser extent, polycarbonate (PC) have found increased use for food packaging. PET has good mechanical properties, excellent transparency and relatively low permeability to gases. PC is tough, stiff, hard and transparent, but has poor gas permeability properties and is still quite expensive.

Unlike glass, plastics are not inert allowing mass transport of compounds such as water, gases, flavours, monomers and fatty acids between a food product, package and the environment due to permeation, migration and absorption. The quality and shelf-life of plastic-packaged food depend strongly on physical and chemical properties of the polymeric film and the interactions between food components and package during storage. Several investigations showed that considerable amounts of aroma compounds can be absorbed by plastic packaging materials, resulting in loss of aroma intensity or an unbalanced flavour profile.[1-7] Absorption may also indirectly affect the food quality by causing delamination of multilayer packages[8,9] or by altering the barrier and mechanical properties of plastic packaging materials.[10] Oxygen permeability through the packaging is an important factor for the shelf-life of many packed foods. Little information is available in literature about the influence of absorbed compounds on the oxygen permeability of packaging materials. Hirose *et al*.[11] reported that the oxygen permeability of LDPE and two types of ionomer increased due to the presence of absorbed D-limonene. Johansson and Leufvén[12] studied the effect of rapeseed oil on the oxygen barrier properties of different polymer packaging materials. They found that amorphous PET remained an excellent oxygen barrier even after storage in rapeseed oil for 40 days. The polyolefins (PP and high-density PE) showed an increased oxygen transmission rate (OTR) after being in contact with rapeseed oil for 40 days. This was

attributed to swelling of the polymer matrix. However, the increase in OTR was not proportional to the amount of absorbed oil.

Sadler and Braddock[13] showed that the oxygen permeability of LDPE was proportional to the mass of absorbed limonene. In another paper, they concluded that oxygen permeability of LDPE and the diffusion coefficients of citrus flavour volatiles in LDPE were related to the solubility of these compounds in the polymer.[14] The increased oxygen permeability of LDPE could only be explained by absorption. Attachment of volatile molecules at the polymer surface (adsorption) might hinder oxygen permeation, which would lower the oxygen permeation, or leave it unchanged. An increased oxygen permeability of LDPE indicated that absorption of volatiles must be responsible for structural changes in the polymer. Flavour absorption can have a major influence on the oxygen permeability of plastic packaging materials, and consequently on the shelf-life of a food product, making it necessary to investigate this important aspect more thoroughly. In this paper, the influence of flavour absorption on the oxygen permeability of LDPE, PP, PC and PET was investigated.

6.2 Materials and methods

6.2.1 Materials

The polymer packaging materials used were low-density polyethylene (LDPE; LDPE 300R; thickness 100 µm; Dow Benelux NV, Terneuzen, The Netherlands), oriented polypropylene (PP; Bicor® MB200; 30 µm; Mobil Plastics Europe, Kerkrade, The Netherlands), polycarbonate (PC; Lexan® 8B35; 75 µm; General Electric Plastics, Bergen op Zoom, The Netherlands) and polyethylene terephthalate (PET; Melinex® 800; 12 µm; DuPont Teijin Films, Luxemburg, Luxemburg).

Decanal and 2-nonanone were purchased from Merck, hexyl acetate from Aldrich and (+)-limonene from Sigma. Tween 80 from Merck was used as an emulsifier, to disperse the flavour compounds in an aqueous phase. Selection of the aroma compounds was based on differences in functional groups, polarity and absorption affinity by the different polymers. Characteristics of the flavour compounds are listed in Table 6.1. Log P represents the hydrophobicity of a flavour compound; a higher Log P means a more hydrophobic compound.

Table 6.1 Characteristics of the flavour compounds used in the model solutions.

Flavour compound	bp (°C)	Log P[a]	Solubility[b] (g/l)	Density (g/ml)	Purity (%)
Limonene	178	4.58	0.0027	0.84	99
Decanal	208	4.09	0.012	0.83	97
2-Nonanone	192	3.30	0.21	0.82	99
Hexyl acetate	168	2.83	0.37	0.88	99

[a] Measure of hydrophobicity, calculated with ACD/Log P v3.6 (www.acdlabs.com)
[b] Solubility at 25ºC in water, calculated with ACD/Aqueous Solubility v4.0 (www.acdlabs.com)

6.2.2 Preparation of flavour model solutions

A flavour model solution was prepared in a stoppered conical flask by dispersing the aroma compounds (100 µl/l each) in 4 g/l aqueous Tween 80. Each flavour compound was added using a micropipet (Micropipette) equipped with a glass capillary tube (Socorex, Lausanne, Switzerland). An Ultra Turrax T25 (IKA-Labortechnik, Staufen, Germany) was used for homogenisation for 2 minutes at 9500 rpm, followed by equilibration overnight in the dark at 40°C.

6.2.3 Exposure conditions

Each polymer specimen (11 x 11 cm) was bent and stapled together with two galvanised staples. Four of these stapled polymer specimens were fully immersed in 1 litre of an equilibrated model solution containing one or more flavour compounds and incubated in the dark at 40°C. Polymer samples immersed in Tween 80 model solution without flavour compounds were used as a blank. Different exposure times were used to achieve different absorbed flavour quantities in the polymers. After exposure, a polymer sample was removed from the model solution, rinsed with ethanol for 10 seconds, and thoroughly wiped with paper tissue to remove excess of the model solution. Polymer samples were divided into two parts. One part was analysed for absorbed flavour compounds using a Large Volume Injection Gas Chromatography (LVI-GC) Ultrasonic ‘in vial’ extraction method. The other part of the sample was placed in a permeation cell to measure the oxygen permeability.

6.2.4 LVI-GC 'in-vial' extraction of the polymer strips

Strips of LDPE (1.5 x 2.0 cm), PP (1.5 x 2.0 cm), PC (1.5 x 11.0 cm) and PET (3.0 x 11.0 cm) were cut in small pieces and immediately placed into a 10-ml vial containing 5 ml n-hexane (Enviroscan, Labscan, Dublin, Ireland). The vials were tightly closed with a Teflon/silicone seal and an aluminium crimp cap. In-vial extraction was carried out for 60 minutes in an ultrasonic bath (Ultrawave, Cardiff, UK). Longer ultrasonic treatment did not achieve better extraction. GC analysis was performed using a LVI-GC system (Ultra Trace^{TM}) (Interscience, Breda, The Netherlands). The background of this technique and equipment used have been described in a previous paper.[1] The following LVI-GC parameters were kept constant for all hexane extracts: helium as carrier gas at a constant flow of 2.3 ml/min; FID detector temperature at 290°C; solvent vapour exit (SVE) temperature at 200°C; oven temperature programme from 50°C (held 10 min) at a rate of 5°C/min to 150°C and further at a rate of 25°C/min to 280°C (held 5 min).

The conditions for the LDPE, PP or PC hexane extracts were: injection volume 30 µl, injection speed 5 µl/s, SVE delay time and secondary cooling time 11 s. The conditions for the PET hexane extracts were: injection volume 200 µl, injection speed 2 µl/s, SVE delay time and secondary cooling time 50 s. Calibration curves (r^2>0.997) were established for each component with the external standard method.

6.2.5 Determination of oxygen permeability

To measure the oxygen permeability of the exposed polymer specimens a set-up based on the isostatic continuous flow technique was developed (Figure 6.1). In the isostatic method the pressure differential across the test film remains constant during the total permeation process. Whereas the high-pressure side (oxygen chamber) remains constant at a certain value, the low-pressure side (nitrogen chamber) is maintained by sweeping the permeated molecules by a continuous flow of carrier gas.[15]

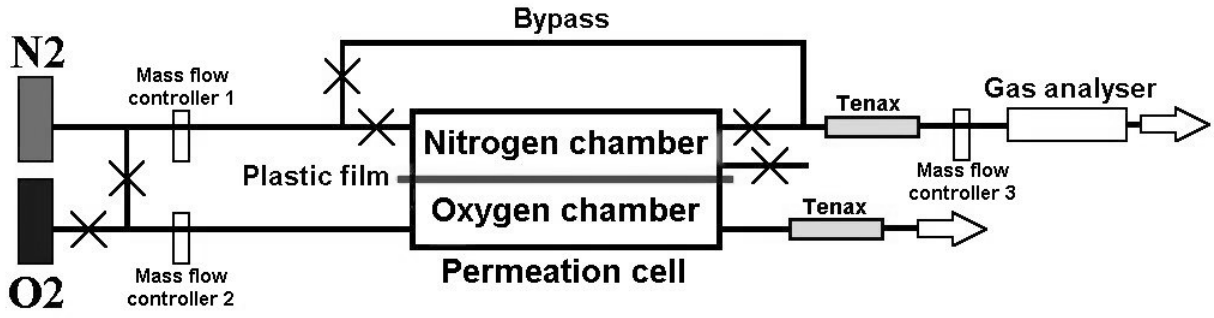

Figure 6.1 Schematic view of the oxygen permeability system.

A stainless steel two-chamber permeation cell was maintained in a temperature controlled cabinet at 25 ± 0.1°C. O-rings were used to ensure airtightness. To remove oxygen, both chambers and polymer film were flushed with dry nitrogen 5.0 (Hoekloos, Schiedam, The Netherlands) for 20 minutes. The flow rate was maintained at a constant flow of 1.5 l/h using calibrated mass flow controllers from Brooks Instruments (Veenendaal, The Netherlands). Initial time was marked when the oxygen 2.5 (Hoekloos) gas stream started to flow through the oxygen chamber. The amount of oxygen permeated per unit of time was monitored continuously for 30 minutes, which was sufficient to reach a maximum permeation. Oxygen concentrations were measured with a Xentra 4100 Gas Purity Analyser (Servomex, Zoetermeer, The Netherlands) equipped with a Zirconia O_2 measuring cell. The gas analyser was calibrated periodically using oxygen-nitrogen mixtures with accurately known oxygen content. Preliminary experiments showed that due to the high operation temperature of the Zirconia measuring cell (±750°C), burning of desorbed flavour compounds occurred, consequently decreasing the oxygen readings. Therefore, tubes filled with Tenax®-TA absorbance (Alltech, Zoetermeer, The Netherlands) were placed between the permeation cell and the gas analyser to prevent entering desorbed flavour compounds into the Zirconia measuring cell. Equal pressure between the two chambers was maintained by placing also Tenax tubes at the exit of the oxygen chamber. The permeability coefficient P was determined directly from the maximum value by:

$$P = \frac{F_{\max} \cdot l}{A \cdot \Delta p}$$

where $F_{\max}$ is the maximum flow of the oxygen (quantity per time), l is the film thickness, A is the area of the film exposed to oxygen and Δp is the driving force or gas pressure gradient through the film.[16] The permeability coefficient is based on two fundamental mass-transfer parameters: the diffusion and solubility coefficient. The diffusion coefficient D is a measure

for the rate of penetrant molecules moving through the barrier, in the direction of lower concentration or partial pressure. Pasternak *et al*.[17] presented an equation to determine the diffusion coefficient (*D*) from the unsteady state portion of the permeation curve:

$$\frac{F_t}{F_{\max}} = \frac{4}{\sqrt{\pi}} X^{1/2} \exp(-X)$$

where F_t is the oxygen flow at time t and $X = l^2/4Dt$. The mathematical method of Newton-Raphson was used to evaluate X as a function of time. The diffusion coefficient is determined from the slope of $1/X$ versus t for values within the range $0.05 < F_t / F_{\max} < 0.95$.[16] The solubility coefficient S describes the amount of the transferring molecules retained or dissolved in the film at equilibrium conditions. When Henry's law of solubility holds, the solubility coefficient S can be calculated from:

$$P = D \cdot S \rightarrow S = \frac{P}{D}$$

6.2.6 Desorption of flavour compounds from PP film

During all oxygen permeability measurements desorption of flavour compounds from the plastic films occurred. The rate of flavour desorption from PP film was investigated after 3 days of exposure to the flavour model solution at 40°C. Preliminary experiments showed that PP reached an absorption equilibrium after 3 days. After 10, 20, 30, 40, 50, 60, 90 and 120 minutes the oxygen permeability experiment was stopped and the film removed from the permeation cell. Two strips (1.5 x 2.0 cm) were cut from the centre of the film to analyse the amount of flavour compounds left.

6.3 Results

6.3.1 PP and LDPE

Table 6.2 presents the absorption values of each individual flavour compound by PP and the influence on the oxygen permeability up to 8 hours of exposure. Limonene showed to have the highest affinity for PP up to a maximum value of 15.76 mg/g PP, followed by decanal with 8.46 mg/g PP, hexyl acetate with 4.56 mg/g PP and nonanone with 4.44 mg/g PP.

Table 6.2 Initial absorption[a] [mg/g PP] of individual flavour compounds by PP and the effect on oxygen permeability P [10^{-18} m^3•m/m^2•s•Pa] at 25°C.

Exposure time (h)	Limonene	P (O_2)	Decanal	P (O_2)	HA[b]	P (O_2)	Nonanone	P (O_2)
0	0.00	2.18	0.00	2.18	0.00	2.18	0.00	2.18
1	2.92	2.41	2.40	2.26	2.36	2.29	0.78	2.08
2	6.60	2.67	4.15	2.36	3.46	2.53	1.56	2.26
3	9.50	3.00	5.20	2.40	4.05	2.61	2.37	2.35
4	11.28	3.19	6.22	2.45	4.29	2.64	3.01	2.47
5	11.22	3.28	7.01	2.56	4.43	2.75	3.84	2.51
6	12.72	3.40	7.49	2.56	4.44	ND[c]	4.17	2.40
7	13.25	3.55	8.05	2.60	4.56	2.77	4.35	2.64
8	15.76	3.79	8.46	2.62	4.49	2.77	4.44	2.63
Slope (x,y)	0.1036		0.0541		0.1335		0.1071	
Intercept (x,y)	2.0934		2.1473		2.1055		2.1005	
R^2 (x,y)	0.9808		0.9691		0.8918		0.8312	
Level of Sign. (df=n-2)	$p < 0.001$		$p < 0.001$		$p < 0.001$		$p < 0.001$	

[a] Average of two replicates; RSD<5%
[b] HA = hexyl acetate
[c] ND = not determined due to leakage

Table 6.2 shows that $P_{PP}(O_2)$ increased with increasing concentrations of absorbed flavour compounds in the polymer. A significant ($p<0.001$) linear relationship between oxygen permeability and flavour absorption was found for all four flavour compounds individually. Significance of correlation was determined using the critical values of the Pearson's product-moment correlation coefficient.[18] Oxygen permeability of PP increased with 73% for limonene, 20% for decanal, 27% for hexyl acetate and 20% for nonanone after 8 hours of exposure. The slope values show that hexyl acetate had the greatest influence on the oxygen permeability per milligram absorbed hexyl acetate, followed by nonanone and limonene, and finally decanal.

Table 6.3 shows the influence of flavour absorption from a model solution containing a mixture of limonene, decanal, hexyl acetate and nonanone on $P(O_2)$, $D(O_2)$ and $S(O_2)$ of PP, LDPE, PC and PET. Table 6.3 shows an increase of absorption and oxygen permeability in time for PP and LDPE. A significant ($p<0.001$) linear increase was found when $P_{pp}(O_2)$ was plotted against the total flavour absorption. After 8 hours of exposure $P_{PP}(O_2)$ increased with $2.79 \cdot 10^{-18}$ m^3•m/m^2•s•Pa (≈130%), $D_{PP}(O_2)$ with $2.84 \cdot 10^{-13}$ m^2/s (≈42%) and $S_{PP}(O_2)$ with $0.20 \cdot 10^{-5}$ m^3/m^3•Pa (≈63%).

Table 6.3 Initial absorption[a] (mg/g) of a mixture of flavour compounds by PP, LDPE, PC and PET and its effect on oxygen permeability P [10^{-18} m^3•m/m^2•s•Pa], diffusivity D [10^{-13} m^2/s] and solubility S [10^{-5} m^3/m^3•Pa] at 25°C.

Polymer	Exposure time	Limonene	Decanal	HA[b]	Nonanone	Total	P (O_2)	D (O_2)	S (O_2)
PP	0h	0.00	0.00	0.00	0.00	0.00	2.14	6.72	0.32
	1h	3.35	2.52	2.39	2.15	10.40	3.05	8.90	0.34
	2h	7.36	4.76	3.26	3.10	18.48	3.76	9.44	0.40
	3h	8.37	5.40	3.50	3.34	20.61	4.28	9.46	0.45
	4h	9.43	6.07	3.78	3.65	22.92	4.44	8.57	0.52
	5h	10.47	6.09	3.49	3.44	23.48	4.53	9.27	0.49
	6h	12.00	6.66	3.60	3.55	25.81	4.68	9.55	0.49
	7h	12.17	6.56	3.52	3.44	25.69	4.77	9.84	0.49
	8h	13.58	6.91	3.66	3.59	27.74	4.93	9.56	0.52
Slope (total, y)							0.1030	0.0913	0.0078
Intercept (total, y)							2.0608	7.2560	0.2937
R^2 (total, y)							0.9894	0.7423	0.8748
Level of significance (df=n-2)							$p < 0.001$	$p < 0.01$	$p < 0.001$
LDPE	0h	0.00	0.00	0.00	0.00	0.00	9.14	83.10	0.110
	1h	1.60	1.45	1.75	1.80	6.60	9.85	89.40	0.110
	2h	2.51	2.30	2.24	2.33	9.37	10.69	98.33	0.109
	3h	3.93	3.53	2.33	2.55	12.33	10.27	90.83	0.113
	4h	4.32	3.83	2.40	2.62	13.16	10.45	91.62	0.114
	5h	2.77	2.52	2.18	2.30	9.77	10.36	100.50	0.103
	6h	4.73	4.09	2.52	2.72	14.07	10.71	96.52	0.111
	7h	5.16	4.20	2.09	2.34	13.79	11.13	98.92	0.112
	8h	5.40	4.46	2.17	2.41	14.44	11.10	95.45	0.116
Slope (total, y)							0.1203	0.7997	0.0003
Intercept (total, y)							9.1604	85.5405	0.1075
R^2 (total, y)							0.8201	0.4537	0.1807
Level of significance (df=n-2)							$p < 0.001$	$p < 0.05$	NS[c]
PC	0d	0.00	0.00	0.00	0.00	0.00	5.14	39.23	0.131
	1d	0.27	0.36	0.38	0.32	1.33	4.75	38.73	0.123
	3d	0.46	0.54	0.56	0.51	2.07	4.87	36.65	0.133
	6d	0.57	0.49	0.72	0.68	2.46	4.43	35.58	0.124
	10d	0.60	0.42	0.81	0.78	2.60	4.65	36.11	0.129
	14d	0.62	0.45	0.83	0.83	2.73	4.54	35.84	0.127
	21d	0.54	0.28	1.01	1.02	2.86	4.59	35.98	0.128
Slope (total, y)							-0.2015	-1.3579	-0.0007
Intercept (total, y)							5.1157	39.6024	0.1292
R^2 (total, y)							0.7505	0.8798	0.0438
Level of significance (df=n-2)							$p < 0.01$	$p < 0.01$	NS
PET	0d	0.000	0.000	0.000	0.000	0.000	0.107	0.913	0.117
	1d	0.043	0.054	0.056	0.050	0.203	0.136	0.863	0.158
	3d	0.034	0.038	0.043	0.039	0.154	0.150	0.847	0.177
	6d	0.037	0.034	0.051	0.047	0.168	0.108	0.856	0.127
	10d	0.030	0.023	0.048	0.044	0.145	0.114	0.915	0.124
	14d	0.022	0.022	0.045	0.040	0.130	0.151	0.888	0.170
	21d	0.021	0.019	0.062	0.058	0.160	0.129	0.894	0.144
Slope (total, y)							0.1186	-0.2551	0.1723
Intercept (total, y)							0.1116	0.9170	0.1217
R^2 (total, y)							0.1664	0.3595	0.2198
Level of significance (df=n-2)							NS	NS	NS

[a] Average of two replicates; RSD<5%

[b] HA = hexyl acetate; [c] NS = not significant

Just like PP, oxygen permeability of LDPE increased significantly ($p<0.001$) due to absorption of flavour compounds (Table 6.3). D_{LDPE} (O_2) showed only a less pronounced ($p<0.05$) linear increase due to flavour absorption and $S_{LDPE}(O_2)$ showed no significant linear relationship.

6.3.2 PC and PET

PC and PET absorbed substantial less flavour compounds than LDPE and PP (Table 6.3). However, hexyl acetate and nonanone showed a higher affinity for PC and PET than limonene and decanal while the latter compounds showed a higher affinity for PP and LDPE. After 21 days of exposure at 40°C, only 2.31 and 0.164 milligram flavour per gram of PC and PET, respectively, were absorbed. Flavour absorption had an opposite effect on the oxygen permeation through PC as was found for PP and LDPE. A significant ($p<0.01$) linear decrease of $P_{PC}(O_2)$ and $D_{PC}(O_2)$ occurred with increasing concentrations of absorbed flavour compounds. Flavour absorption had no significant effect on the oxygen solubility of PC. No significant effect was found on the oxygen permeability, diffusivity and solubility of PET due to flavour absorption.

6.4 Discussion

6.4.1 PP and LDPE

Figure 6.2 gives a good picture of the influence of the total amount of flavour absorption on the oxygen permeability of all four investigated polymers. PP's and LDPE's increased oxygen permeability in the presence of absorbed flavour compounds indicated that molecular changes occurred in the polymer network.

Several researchers reported that swelling of a polymer by a permeant (i.e. plasticising) greatly increased the diffusivity. During the absorption process molecules are absorbed in the free volume ('holes') which is always present in the amorphous regions. Diffusion and a slow relaxation of the polymer, reducing the intercatenary forces and even promoting polymer swelling control the rate of absorption. This further enhances the rate of diffusion,

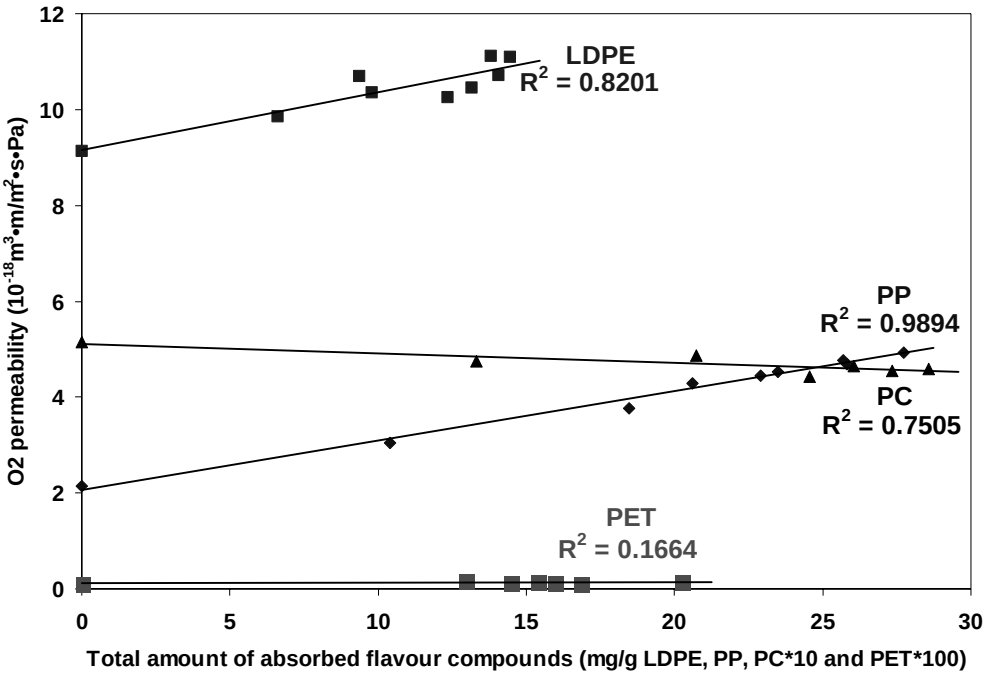

Figure 6.2 Influence of total flavour absorption on oxygen permeability of PP, LDPE, PC and PET at 25°C.

which further influences the relaxation. As a result, the permeation of one component affects the permeation of another component, i.e. the plasticising effect within the polymer matrix becomes apparent.[19,20]

Absorbed water has a similar effect on the permeability of some hydrophilic polymers, such as ethylene vinyl alcohol (EVOH) and most polyamides. Water molecules absorbed at high relative humidities are believed to combine with hydroxyl groups in the polymer matrix and weaken the existing hydrogen bounds between polymer molecules. As a result, the interchain distances increase and thus free volume, facilitating the diffusion of oxygen and perhaps other gases. The presence of water in the hydrophilic polymer matrix not only influences how a permeant is sorbed and diffused, it also leads to depression of the glass transition temperature (Tg) of the polymer due to the plasticising effect of water. When the Tg drops below storage temperature, a substantial increase in oxygen permeability is expected.[21,22] Krizan *et al*.[23] reported that free volume in a polymer is the dominant factor in determining the permeation properties. A plot of the log of the oxygen permeability coefficients versus the reciprocal of the specific free volume showed a good linear relationship. Also Sadler and Braddock[13] reported that the oxygen permeability was proportional to the mass of absorbed limonene. Differences in slope values (Table 6.2) indicate that the increase of oxygen permeability is related to the plasticising efficiency. The specific molecular composition of a

flavour compound seems to play a more important role than the mass of absorbed flavour compounds. Each individual absorbed flavour compound caused swelling of PP; i.e. increased the specific free volume.

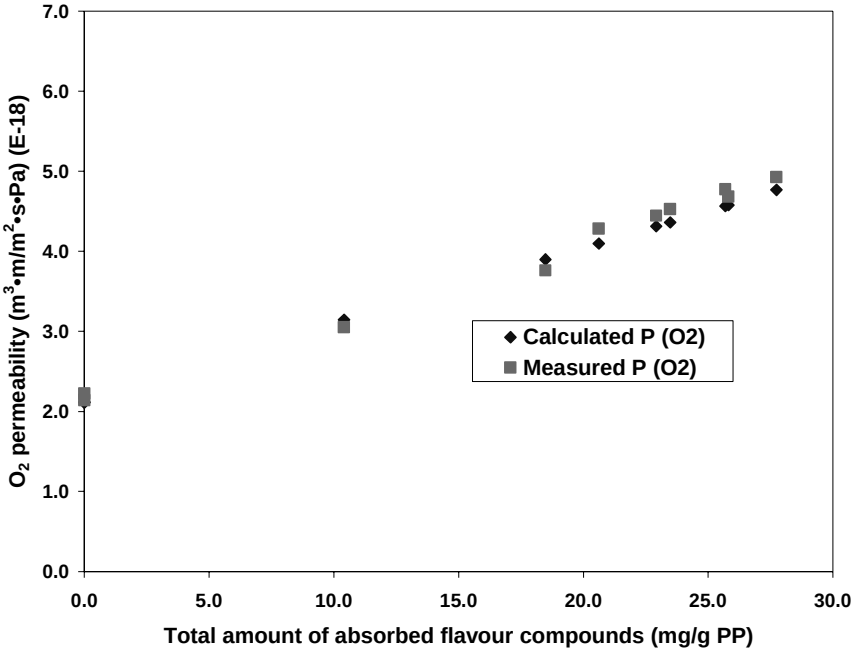

Figure 6.3 Measured and calculated oxygen permeability values of PP at 25°C.

Using the slope values of each flavour compound and the average intercept from Table 6.2, the oxygen permeability was calculated using the absorption data presented in Table 6.3:

P_{pp} (O_2) = 0.1036 [limonene] + 0.0541 [decanal] + 0.1335 [hexyl acetate] + 0.1071 [nonanone] + 2.1117.

Figure 6.3 shows that the measured and calculated oxygen permeability values are almost equal. This shows that the oxygen permeability is related to the sum of the changes in specific free volume caused by each absorbed flavour compound (additive effect).

6.4.2 Desorption of flavour compounds from PP film

Figure 6.4 shows the desorption of flavour compounds from PP film during a permeation measurement. In the first 20 minutes of the experiment (=flushing period) 28% of the absorbed flavour compounds desorbed from the PP film. At the time of reaching the

maximum oxygen flow, an absolute amount of 11.4 mg (=36%) of flavour compounds was evaporated. After a measuring period of 120 minutes, only 38% of the initial absorbed quantity remained in the PP film. The permeation curve in Figure 6.4 shows that after

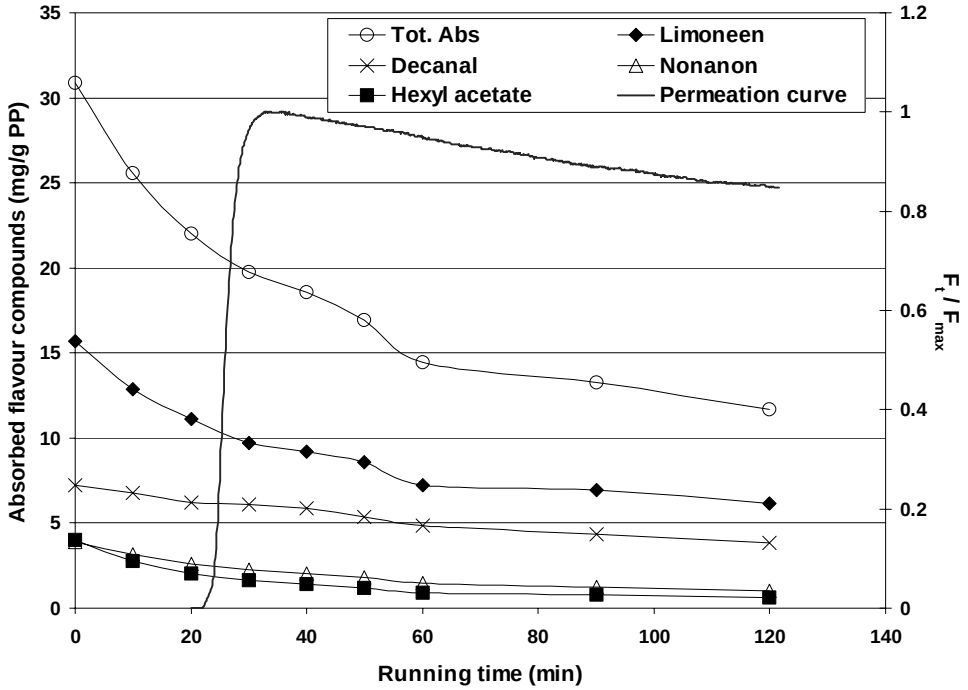

Figure 6.4 Oxygen permeation curve and amount of flavour compounds in PP during permeability measurement at 25°C.

reaching a maximum a steady decrease of F_t/F_{max}, i.e. oxygen permeability, occurred due to the desorption of flavour compounds from the PP film. This effect was not observed for the blanks. It was suggested that as soon as the desorption process of flavour compounds from the PP film started, the polymer network tried to regain its original structure, i.e. proportional decrease of the oxygen permeability. If we could measure the oxygen permeability at t=0, the real oxygen permeability values would be expected to be higher than the values given in Table 6.2 and 6.3.

6.4.3 PC and PET

Rubbery polymers (LDPE and PP) have very short relaxation times and respond very rapidly to stresses that tend to change their physical conditions. Glassy polymers (PC and PET) have very long relaxation times. Penetrant (molecules) can thus potentially be present in 'holes' or irregular cavities with very different intrinsic diffusional mobilities.[24] Hernandez-Muñoz *et*

al.[20] reported that there are two possible effects of absorbed flavour compounds on oxygen mass transport: (1) flavour compounds and oxygen compete for the same sites, reducing the solubility of oxygen since many sites are already occupied and (2) the flavour compounds swell the polymer, opening the structure and increasing polymer free volume, i.e. oxygen transport. The presence of holes is assumed for rubbery polymers as well as for glassy polymers. 'Hole filling' is suggested as an important sorption mode above as well as below Tg, with one crucial difference between the sorption mechanisms in the rubbery and glassy regions: hole saturation does not occur in the rubbery state because new holes are formed to replace those filled with penetrant molecules.[24] Landois-Garza and Hotchkiss[25] reported that the presence of water molecules in the polymer matrix occupied 'holes' that otherwise would be available for the diffusion of permeant molecules, effectively increased the length of the viable diffusion paths, and diminished the permeant diffusivity.

The linear decrease of the oxygen diffusivity of PC due to flavour absorption suggests that 'hole filling', resulting in an increased oxygen diffusion pathway, was also found in this study. However, the oxygen permeability of PET, which is also in its glassy state at 25°C, was not significantly affected by absorption of flavour compounds. Because of the low oxygen permeability of PET which was close to the detection limit of the oxygen analyser a significant effect of flavour absorption on oxygen permeability cannot be ruled out. A more sensitive oxygen analyser or a smaller permeation cell should be used in order to investigate the influence of absorption of flavour absorption on the oxygen permeability of PET.

6.5 Conclusions

Data show that flavour absorption increased oxygen permeability of PP and LDPE with 130% and 21% after 8 hours of exposure to various flavour compounds. Because of the higher oxygen permeability a reduction in the shelf-life of oxygen sensitive products, which are packed in LDPE or PP and contain the tested flavour compounds (such as orange juice and apple juice) can be expected. Furthermore, flavour absorption has probably a positive effect on the shelf-life of oxygen sensitive products packed in PC, because of the reduction in oxygen permeability with 11% after 21 days of exposure to various flavour compounds. Oxygen permeability of PET was not influenced by the presence of flavour compounds, meaning that PET remained a good oxygen barrier. One should realise that the concentrations

of flavour compounds in real food products are usually substantially lower, with the exception of limonene, than the concentrations used in this study. Therefore, the observed effects may be less or even not significant in foods and beverages.

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7

Influence of flavour absorption by LDPE, PC and PET food packaging materials on taste perception of a model solution and orange juice

Abstract

The influence of flavour absorption by low-density polyethylene (LDPE), polycarbonate (PC) and polyethylene terephthalate (PET) on taste perception of a model solution containing 7 flavour compounds and orange juice in glass bottles was studied with and without pieces of the respective plastic films after dark storage at 20°C. Due to absorption the amount of flavour compounds in the model solution exposed to LDPE decreased substantially. From the model flavour solution valencene was almost completely absorbed by LDPE, followed to a lesser extent by decanal, hexyl acetate, octanal and nonanone. Less flavour compounds were absorbed from the model solution by PC and PET. In contrast to LDPE, valencene was absorbed in the lowest amounts and decanal to the highest. Limonene was readily absorbed from orange juice by LDPE, while myrcene, valencene, pinene and decanal were absorbed in smaller quantities. Only three flavour compounds were absorbed from orange juice by PC and PET in very small amounts; limonene, myrcene and decanal. Although flavour content between controls and polymer treated samples differed substantially, the loss of flavour compounds due to absorption by LDPE, PC and PET did not influence taste perception of a model solution and orange juice significantly up to 29 days of dark storage at 20°C as determined by triangular taste panel tests.

This chapter has been submitted as:

Van Willige RWG, Linssen JPH, Legger-Huysman A and Voragen AGJ, *Food Addit and Contam.*

7.1 Introduction

The quality of juices, aseptically packed in laminated cartons, has been the subject of extensive research during the last decades. Loss of organoleptic characteristics during storage has been commonly observed.[1-3] Most aseptically filled juices are packed in low-density polyethylene (LDPE) laminated carton packs, such as Tetra Brik® and Combibloc®. Several investigations have shown that considerable amounts of flavour compounds can be absorbed by LDPE.[4-6] Food industries therefore often correct this absorptive effect by adding excess flavours to the food for keeping taste and flavour acceptable for consumers until the end of the product's shelf-life.[7]

While flavour absorption may be high enough to affect the sensory quality of a packaged food, only a few authors have conducted sensory tests to go along with the analytical results.[2,8-10] Durr *et al.*[11] showed that absorption of d-limonene up to 40% did not affect the sensory quality of orange juice during 3 months storage at 20°C. They suggested that d-limonene contributed scarcely to the flavour of orange juice. Moreover, they considered limonene absorption even as an advantage, since limonene is known as a precursor to off-flavour compounds. They also reported that the storage temperature was the main quality parameter for the shelf-life of orange juice. Kwapong and Hotchkiss[8] found that assessors were able to detect a significant difference in odour due to absorption of citrus essential oils from aqueous model solutions by LDPE strips using a triangle sniffing test. Moshonas and Shaw[2] noticed significant reduced flavour scores using a sensory panel for a commercial aseptically packaged orange juice stored for 6 weeks at 21°C and 26°C. They concluded that the combined loss of limonene due to absorption and the increase of potential off-flavour compounds undoubtedly contributed to the detected flavour changes. Mannheim *et al.*[9] found that the product shelf-life of orange and grapefruit juices was significantly shorter in LDPE laminated cartons than in glass jars. This was accompanied by a loss of ascorbic acid and an increase in brown colour. A 40% decrease of limonene was found; other volatiles were not assayed. In a triangle test they revealed a difference in taste after ten weeks of storage at 25°C. Sharma *et al.*[10] reported that polyethylene and polypropylene contact did not cause perceptible changes in sensory quality of fruit squash (orange and lemon) and beverages (mango, orange and blue grapes). Pieper *et al.*[12] stored orange juice in glass bottles and in LDPE laminated cardboard packages at 4°C for 24 weeks. Absorption of d-limonene up to 50% and small amounts of aldehydes and alcohols by the packaging materials did not affect

the sensory quality of orange juice significantly. The reason could be the low storage temperature. Sadler *et al.*[13] reported that no evidence was found that flavour absorption directly altered sensory characteristics of orange juice through general or selective absorption of volatile compounds by LDPE, polyethylene terephthalate **(**PET) and ethylene vinyl alcohol (EVOH) after 3 weeks of storage at 4.5°C. Marin *et al.*[14] exposed orange juice to LDPE and an ionomer (ie. Surlyn). The polymers absorbed more than 70% of the limonene content in 24 hours at 25°C. However, results from gaschromatography-olfactometry (GCO) analysis indicated that limonene possessed only trace odour activity. Furthermore, the plastic polymers did not alter the odour-active components present in orange juice substantially.
In a review Gremli[15] stated that, from all the published data, there is ample evidence that flavour compounds migrate from beverages and foods into plastic packaging materials. However, investigations about the relevance of the loss of flavour compounds for the sensory quality of a product are insufficient and sometimes contradictory because flavour alteration depends on many parameters, such as storage temperature and type of packaging material. Therefore, investigations regarding the effect of flavour absorption on sensory quality of a product should be carried out at ambient temperature (i.e. usual storage conditions of aseptic packs), because the rate and amount of flavour absorption by packaging materials increases with increasing temperature.[5] Furthermore, it is important that the polymer treated and untreated (=control) samples are similar packed, i.e. a sensory evaluation should be made between packaging systems with a similar oxygen permeability (i.e. glass-glass, and not glass-laminated carton). In the present study the influence of flavour absorption by LDPE, PET and polycarbonate (PC) food packaging materials on taste perception of a model solution and orange juice during 29 days of dark storage in glass bottles at 20°C was investigated.

7.2 Materials and methods

7.2.1 Materials

The polymer packaging materials used were low-density polyethylene (LDPE; LDPE 300R; thickness 100 µm; Dow Benelux NV, Terneuzen, The Netherlands), polycarbonate (PC; Lexan® 8B35; 75 µm; General Electric Plastics, Bergen op Zoom, The Netherlands) and

polyethylene terephthalate (PET; Melinex® 800; 75 µm; DuPont Teijin Films, Luxemburg, Luxemburg). Glass bottles (1 litre) were of the type normally used for mineral water. Octanal, decanal, ethyl butyrate (EB), and 2-nonanone were purchased from Merck (Darmstadt, Germany), linalool and valencene from Acros Organics (Fisher Scientific UK Ltd, Loughborough, UK), and hexyl acetate (HA) from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA). Low substituted carboxymethylcellulose (CMC, AKU LZ 855; SD=0.85) from Akzo (Arnhem, The Netherlands) was used as a stabiliser in the model solution. Orange juice was reconstituted from concentrate to 11.7° Brix in a commercial company.

7.2.2 Preparation of the model solution

A flavour stock solution was prepared in a stoppered conical flask by dissolving ethyl butyrate, hexyl acetate, octanal, decanal, linalool, 2-nonanone, and valencene in 10 g l^{-1} aqueous CMC in a concentration of 100 µl l^{-1} each. Flavour compounds were selected based on functional groups and their presence in fruit juices. Flavour components were added using a micropipet (Micropipette) equipped with a glass capillary tube (Socorex, Lausanne, Switzerland). An Ultra Turrax T25 (IKA-Labortechnik, Staufen, Germany) was used for homogenisation for 10 minutes at 13500 rpm. In a commercial company the final model solution was prepared by adding 1 litre of the flavour stock solution to 49 litres of an aqueous solution containing 1 kg of saccharose (Merck) and 20 grams of citric acid monohydrate (Merck).

7.2.3 Filling of the bottles and addition of the plastic strips

In a commercial company the glass bottles were filled with 1 kilogram of model solution or orange juice. After filling, all bottles were closed with a screw cap and pasteurised using the following temperature programme; temperature rise from 25°C to 80°C in 15 min, an isothermal hold for 4.5 min, and cooling down to 25°C in 20 min. In a laminar-flow cabinet, strips (10 x 5 cm) of LDPE, PC and PET were sterilised in 70% (v/v) ethanol for several minutes and subsequently dried in sterile air. Six polymer strips of LDPE, PC or PET

(area/weight ratio: 600 cm^2/kg of model solution or orange juice, i.e. comparable with the food-packaging contact area in a 1 litre package) were aseptically transferred to each bottle of model solution or orange juice and incubated in the dark at 20°C during 29 days. Preliminary investigations showed that total plate counts on Tryptone Soya Agar (TSA) were minimal (<10 cfu/ml) for both model solution and orange juice after exposure to the polymer strips for 29 days at 20°C. Controls were free of polymer strips, but were subjected to all treatment and storage steps as described. The amounts of flavour compounds in the polymer strips, orange juice and model solutions were analysed using Large Volume Injection Gas Chromatography (LVI-GC) and static headspace GC, respectively.

7.2.4 LVI-GC 'in-vial' extraction of the polymer strips

After exposure the polymer strips were removed from the model solution and orange juice, rinsed with ethanol for 10 seconds, and thoroughly wiped with paper tissue to remove excess of the liquid. From the polymer strips smaller strips of LDPE (1.5 x 2.0 cm), PC (1.5 x 10 cm), and PET (3.0 x 10 cm) were cut in triplicate. These smaller strips were cut in pieces and immediately placed into 10-ml vials containing 5 ml n-hexane (Enviroscan®, Labscan, Dublin, Ireland). The vials were tightly closed with a Teflon/silicone seal and an aluminium crimp cap. In-vial extraction was carried out for 60 minutes in an ultrasonic bath (Ultrawave, Cardiff, UK). Longer ultrasonic treatment did not achieve better extraction. The extracts were analysed by a LVI-GC system (Ultra Trace™, Interscience, Breda, The Netherlands) as previously described (Chapter 2).[16] Calibration curves (r^2>0.998) were established for each component with the external standard method. A relative standard deviation (RSD) of less than 10% was found between triplicate determinations. Peaks were identified by comparison of retention times of peaks from authentic standards.

7.2.5 Static Headspace GC extraction of model solutions and orange juice

After each exposure period the concentration of flavour compounds in samples (3 ml) of model solution and orange juice was determined in triplicate using static headspace GC. The headspace sampler, cold trap and GC conditions used are given in Table 7.1. GC equipment

used has been previously described.[16] The different components were identified by comparison of retention times with those of standards and by spiking of the model solution or orange juice with flavour compounds. Calibration curves (r^2>0.998) with the intercept set at zero were established for each component by injecting five different concentrations of each flavour component to the orange juice or model solution.

Table 7.1 Static headspace sampler, cold trap and GC conditions.

Conditions	Value
Automated headspace sampler	
Temperature sampling tray	4°C
Equilibrium time	15 min
Equilibrium temperature	60°C
Stirring speed (10s on; 10s off)	2000 rpm
Temperature of injection syringe	70°C
Volume of headspace injected[1]	2000 µl (50 µl for limonene quantification)
Cold trap conditions	
Cooling temperature	-75°C
Time	20 s
Desorption temperature	240°C
GC conditions	
Carrier gas	Helium (30 kPa)
Injector temperature	200°C
FID detector temperature	250°C
Oven programme	40°C (4') => 2°C min^{-1} => 80°C => 10°C min^{-1} => 200°C (4')

7.2.6 Sensory evaluation

Sensory evaluations were carried out on model solution and orange juice samples using duplicate triangle testing to determine differences in flavour between the controls and the samples exposed to LDPE, PC and PET food packaging materials. From a group of 27 assessors, 8 males and 19 females between 19 and 53 years old, 22-26 untrained assessors participated in the different sessions. Samples were sensory evaluated in 5 sessions, i.e. after 1, 8, 15, 22 and 29 days of storage. Equal volumes of samples (12 ml) were presented to the assessors at room temperature in sensory evaluation booths. Samples were offered in glass

jars, covered with aluminium foil and closed with screw caps. Each assessor was presented with three samples, of which two were identical, and asked to indicate which sample differed in taste. An unlimited time was available to evaluate the samples. For each session, samples were assessed twice in a randomised order for each assessor. The numbers of correct responses were determined, and considered significantly different if they differed at a $P< 0.05$ level of significance.[17]

7.3 Results and discussion

7.3.1 Flavour absorption and sensory evaluation of the model solution

Changes in quantities of flavour compounds in the model solution samples during 29 days of dark storage at 20ºC are given in Figure 7.1. Figure 7.2 shows the absorbed amounts of flavour compounds from the model solution by LDPE, PC and PET. Due to degradation a decrease of valencene (52%), decanal (49%), octanal (19%), nonanone (15%) and hexyl acetate (14%) was found in the control (Figure 7.1A) after 29 days of storage.

In the presence of LDPE (Figure 7.1B) a further decrease of above flavour compounds in the model solution was noticed. Valencene even disappeared completely, which means that this compound was strongly absorbed by LDPE. Figure 7.2A shows that valencene was absorbed at a level of 0.61 mg/g LDPE after 15 days of storage, followed by decanal at 0.33 mg/g LDPE, HA+octanal at 0.1 mg/g LDPE and nonanone at 0.07 mg/g LDPE. It should be noted that hexyl acetate and octanal were not properly separated by the LVI-GC system. In order not to lose any results a standard curve was established from the peak area of the two not separated components. The absorption behaviour of PC and PET was different to that of LDPE. Valencene was absorbed in the highest quantities by LDPE and by PC and PET to the lowest extent.

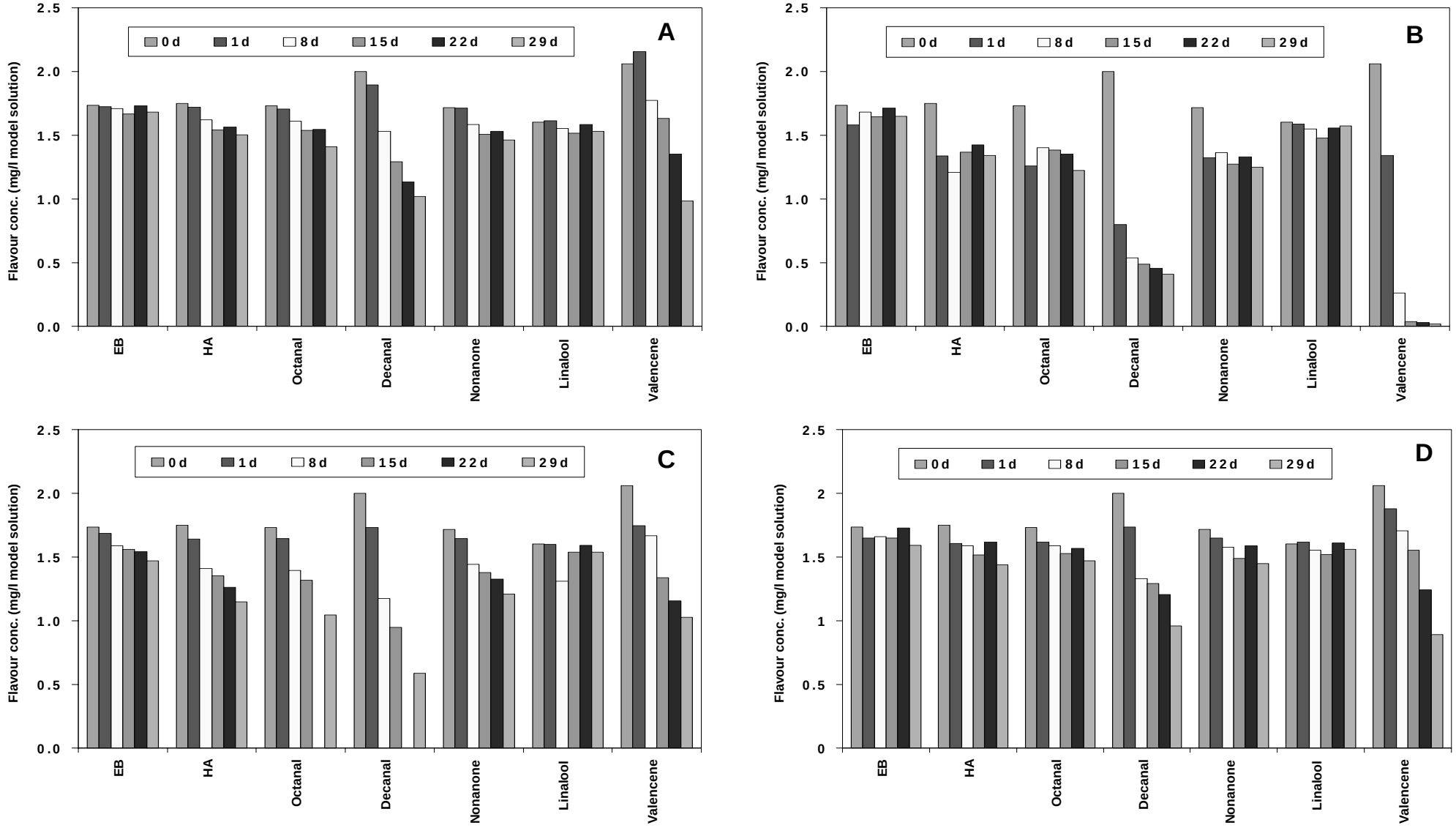

Figure 7.1 Effect of packaging material on the concentration of flavour compounds (EB=ethyl butyrate and HA=hexyl acetate) in the model solution during 29 days of dark storage at 20°C. (A) control, (B) LDPE, (C) PC, and (D) PET.

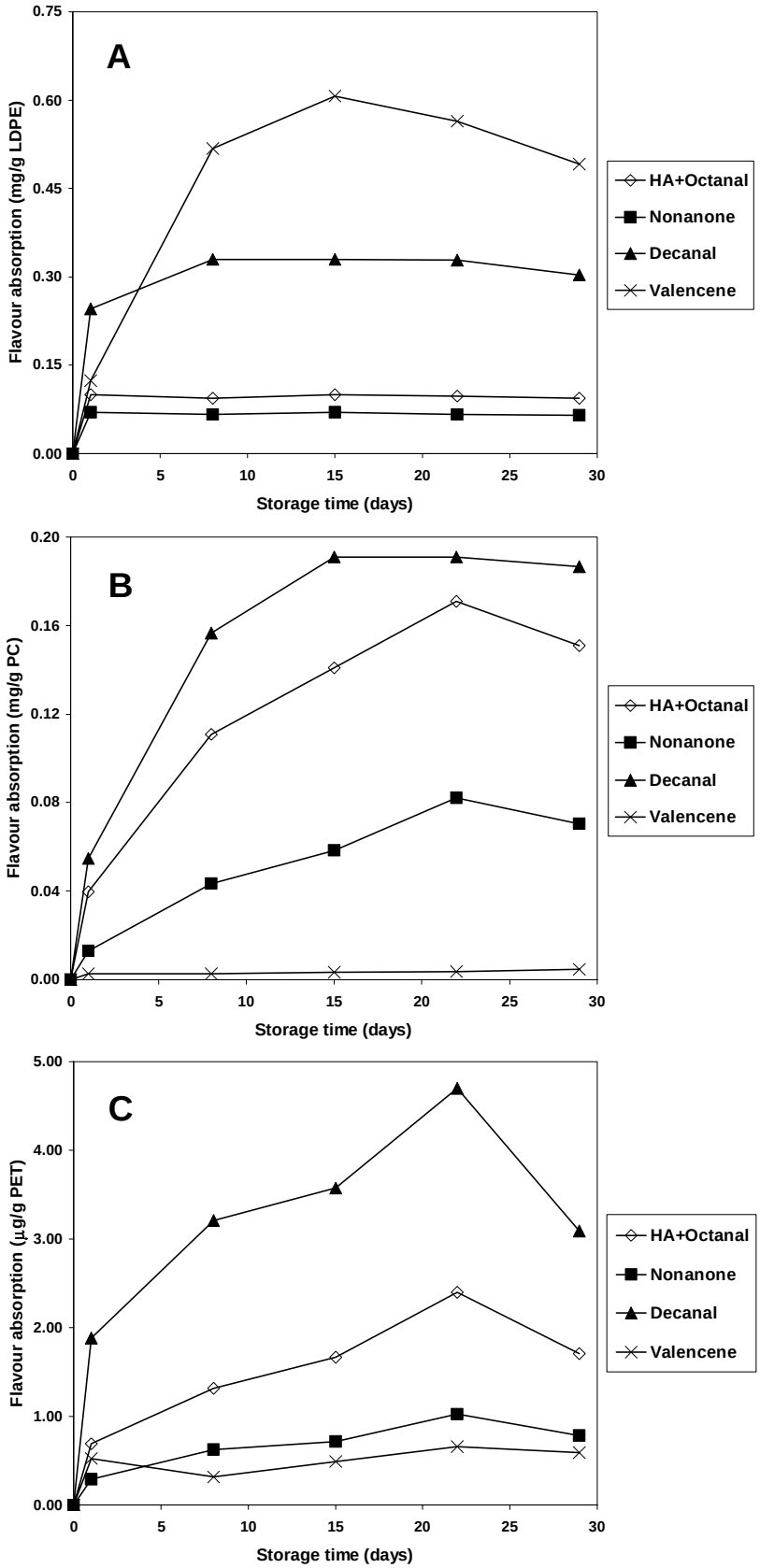

Figure 7.2 Concentration of flavour compounds (HA = hexyl acetate) in (A) LDPE, (B) PC, and (C) PET after exposure to the model solution during 29 days of dark storage at 20°C.

Table 7.2 shows the results of the sensory evaluations of the model solutions. No significant differences were found by the assessors, except for the model solution that was exposed to PC for 22 days. Instrumental analysis showed that the concentration of octanal and decanal in the model solution exposed to PC was reduced to zero after 22 days of storage (Figure 7.1C). Two new flavour compounds were identified, octanol and decanol. This reduction of octanal and decanal to octanol and decanol was only observed in that particular bottle. The presence of a yeast (insufficient pasteurisation) or maybe a catalyst (dirty bottle) could be the reason for this reaction. Grab *et al.*[18] found comparable results in functional drinks containing orange, lemon and lime flavours. They reported a reduction of aldehydes to the corresponding alcohols, leading to an unbalanced and unacceptable soapy flavour profile. They also could not identify the real reason for this unusual reduction process. However, this significant difference cannot be attributed to flavour absorption by PC, but only to the formation of octanol and decanol. Because no other significant differences were found, it can be concluded that flavour absorption does not affect the taste perception of the investigated model solution.

Table 7.2 Duplicate triangle test results of a model solution and orange juice exposed to LDPE, PC and PET for 29 days at 20ºC.

Storage Time /	Correct responses Model solution			Correct responses Orange juice		
Level of Significance	LDPE	PC	PET	LDPE	PC	PET
Day 1 (n=26, 14=significant)	10	7	4.5	12	5	9.5
Level of significance	NS[1]	NS	NS	NS	NS	NS
Day 8 (n=25, 13=significant)	9	10	12	10	7	9.5
Level of significance	NS	NS	NS	NS	NS	NS
Day 15 (n=24, 13=significant)	8	6.5	8	9.5	7.5	8
Level of significance	NS	NS	NS	NS	NS	NS
Day 22 (n=24, 13=significant)	6	**14**	5	9.5	4.5	8
Level of significance	NS	**P<0.05**	NS	NS	NS	NS
Day 29 (n=22, 12=significant)	5	5.5	8	9.5	7.5	10.5
Level of significance	NS	NS	NS	NS	NS	NS

[1] NS = not significant at the 5% level of significance.

7.3.2 Flavour absorption and sensory evaluation of orange juice

Figure 7.3 shows the changes in quantities of flavour compounds in the orange juice samples during 29 days of dark storage at 20ºC. Figure 7.4 shows the absorbed amounts of flavour

compounds from orange juice by LDPE, PC and PET. Figure 7.3A (=control) shows that octanal and decanal were not stable in orange juice during storage. With increasing storage time the concentration of octanal and decanal in orange juice decreased with 60% and 46%, respectively, probably due to degradation. Similar results for octanal, decanal, limonene and EB were also observed in orange juice by other researchers.[2,11,19] However, valencene was more stable in orange juice than in the model solution. This was probably due to the more complex matrix of orange juice compared to the simple matrix (water and CMC) of the model solution. The concentration of all other investigated flavour compounds remained relatively constant. In the presence of LDPE (Figure 7.3B) a rapid decrease in concentration of pinene (46%), myrcene (38%), valencene (18%) and limonene (44%) in orange juice was observed during storage. Figure 7.4A shows that LDPE readily absorbed limonene at a level of 13.5 mg/g LDPE, followed by myrcene at 0.26 mg/g LDPE, valencene at 0.21 mg/g LDPE, pinene at 0.089 mg/g LDPE and decanal at 0.035 mg/g LDPE. Orange juice exposed to PC and PET (Figure 7.3C and 7.3D) showed an almost identical flavour profile as that of the control sample after 29 days of storage. Only three flavour compounds could be extracted from the PC and PET strips in very small quantities; limonene, myrcene and decanal (Figure 7.4B and 7.4C).

Table 7.2 shows the results of the sensory evaluations of orange juice. Although a substantial decrease in concentration of several flavour compounds due to absorption was observed in the instrumental part, no significant differences were found in taste perception between polymer treated samples and controls. These results indicate that flavour absorption does not seriously affect the overall orange juice flavour.

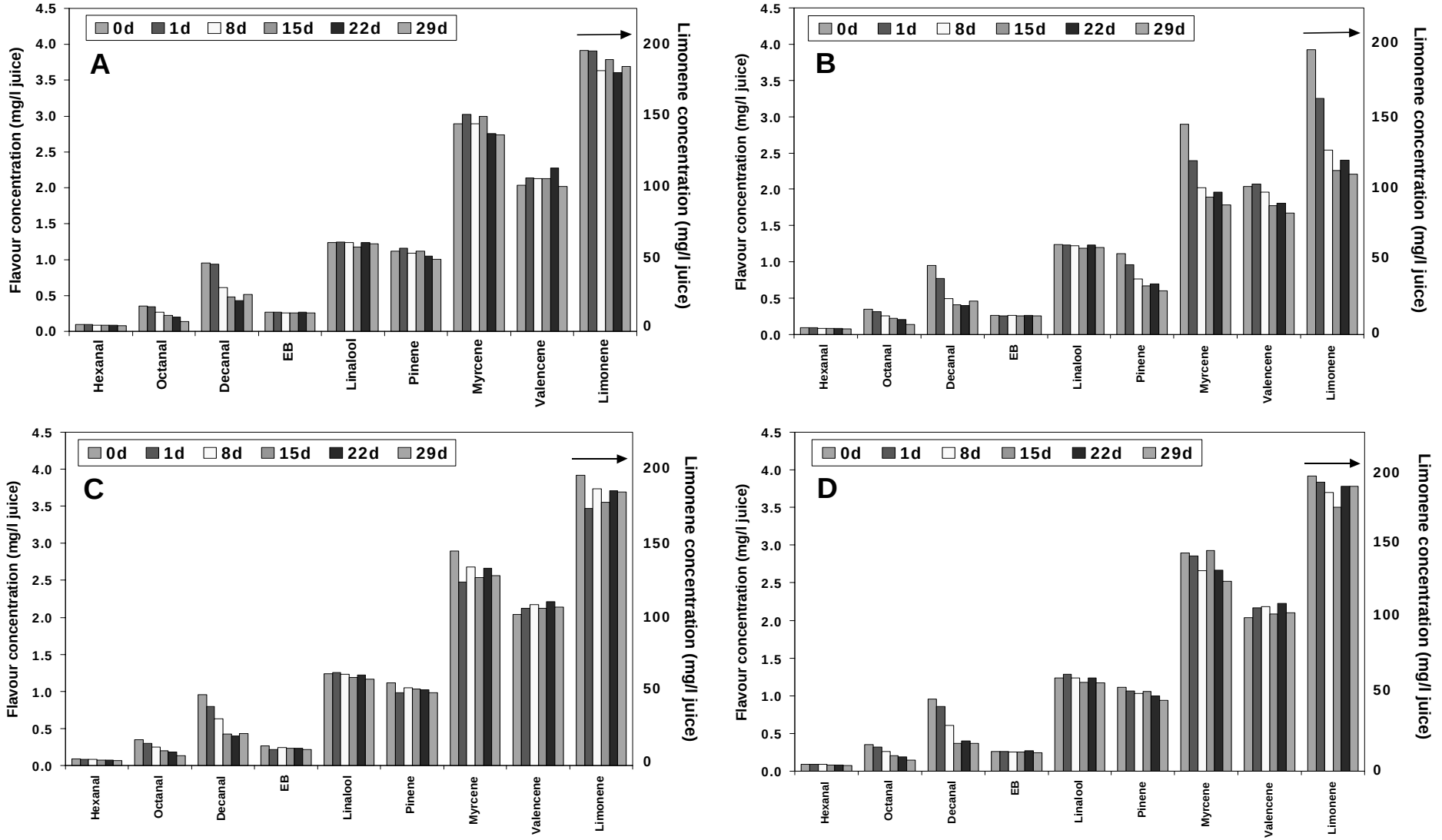

Figure 7.3 Effect of packaging material on the concentration of flavour compounds (EB=ethyl butyrate) in orange juice during 29 days of dark storage at 20°C. (A) control, (B) LDPE, (C) PC, and (D) PET.

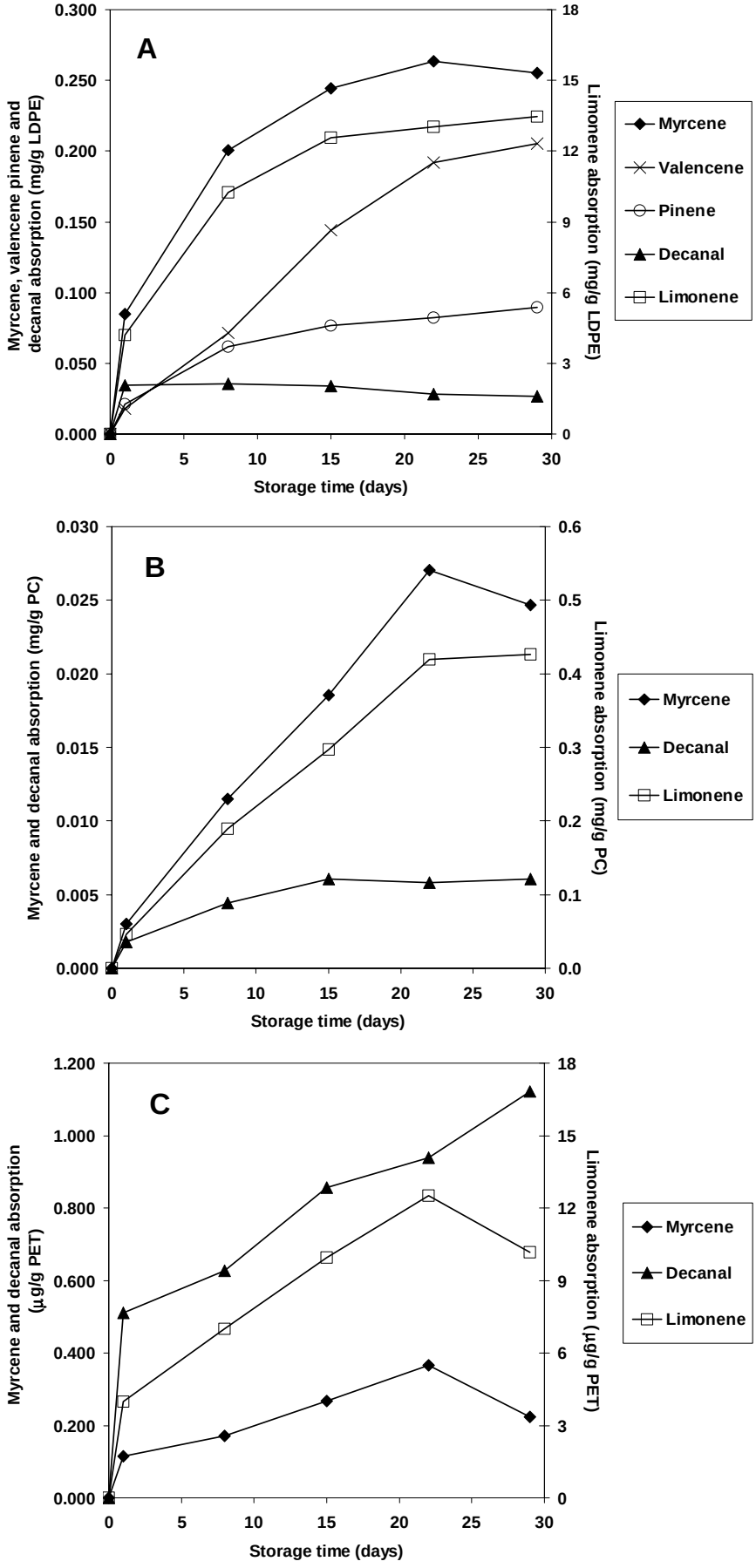

Figure 7.4 Concentration of flavour compounds in (A) LDPE, (B) PC, and (C) PET after exposure to orange juice during 29 days of dark storage at 20°C.

7.4 Conclusions

Instrumental analysis showed substantial differences in flavour content between control and polymer treated samples. However, no significant differences in taste perception of a model solution or orange juice were observed after 29 days of dark storage at 20°C. A possible change of flavour during storage of a model solution or orange juice is not caused by absorption of flavour compounds into LDPE, PC and PET food packaging materials. It is more likely that other mechanisms play a more important role, such as chemical degradation resulting in a development of off-flavour components. Storage temperature remains the single most important factor in delaying flavour loss and achieving satisfactory shelf-life and quality.[19]

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8

Concluding remarks and summary

8.1 Research motives

Flavour compounds give foods and beverages their distinct individual identity and are the basis upon which consumers decide what product they will buy and consume repeatedly. It is important that food products keep their flavour as good as possible before they reach the consumer. Plastic packaging materials can directly and indirectly contribute to flavour changes, because plastics are less inert than glass and metals and can interact with foodstuffs in a variety of ways.[1] The most important food packaging interactions are: permeation, migration and absorption. Much work has been done on the migration of low molecular weight compounds from the polymer into foods and their possible toxicity. Also several studies on permeability and absorption of gases and water vapour by polymers are available. However, less studies deal with absorption of flavour compounds into polymer packages[2-6], its effect on packaging integrity[7-11], and the possible effects on product quality.[12-16] Literature about flavour absorption often includes contradictory findings (e.g. the influence on taste perception). Moreover, it becomes apparent that the mechanisms behind flavour absorption by polymers are not yet fully understood. In this thesis different aspects of flavour absorption by plastic packaging materials have been studied: the influence of the food matrix and storage conditions on the extent of flavour absorption, and the influence of flavour absorption on the oxygen permeability of the polymer and the sensory quality of a product.

8.2 Effect of food matrix

Absorption of flavour compounds into plastic packaging materials is influenced by interactions of the flavour compounds with the food matrix. Flavours may be dissolved, adsorbed, bound, entrapped, encapsulated or retarded in diffusion through the matrix by certain food components. The relative importance of each of these mechanisms varies with the properties of the flavours (functional groups, molecular size, shape, volatility, polarity, etc) and the chemical and physical properties of the components in the food matrix.[17,18]

The effects of differences in food matrices on the absorption of four flavour compounds, limonene, decanal, linalool and ethyl 2-methylbutyrate (E2MB), into linear low-density polyethylene (LLDPE) were studied by using a Large Volume Injection GC ‘in vial’ extraction method (Chapters 2 and 3). The effect of the presence of proteins, carbohydrates

and oil were investigated. Protein systems included β-lactoglobulin and casein; carbohydrate systems included pectin, carboxymethylcellulose (CMC), lactose and saccharose, and lipid systems included oil in water emulsions. Also some combined models, oil/casein and oil/pectin, were investigated as well as some real food products, skim milk and whole milk.

It was found that β-lactoglobulin interacted irreversibly with decanal and therefore suppressed decanal absorption by LLDPE by more than 50% after 14 days of exposure. Casein was able to bind limonene and decanal, resulting in a decreased absorption of 40% and 90%, respectively. The presence of CMC and pectin (thickening agents) slowed down diffusion of limonene and decanal from the food matrix to LLDPE, and consequently the absorption rate of limonene and to a lesser extent of decanal. Due to a 'salting out' effect lactose and saccharose increased absorption of linalool and E2MB. Lactose, saccharose and CMC, however, decreased the absorption of decanal after 14 days of exposure, probably due to an interactive effect between a sugar(residue) and decanal.

The presence of oil influenced absorption of the flavour compounds substantially: a relative small amount of oil (50 g/l) decreased the amount of flavour absorption with approximately 90%. Solubilization of the apolar flavour compounds into the oily phase made only the remaining flavour compounds solved in the aqueous phase available for absorption into the polymer. Due to a 'salting out' effect, absorption of the less apolar E2MB first increased with increasing oil concentration, but decreased at higher oil concentrations (> 2.5 g/l). The oil/casein and oil/pectin models showed a similar effect. The presence of oil influenced the level of absorbed flavour compounds to a much greater extent than proteins (e.g. casein) or carbohydrates (e.g. pectin).

The findings of these model systems were confirmed with some real food products. However, the low amount of fat (1.11 g/l) in skim milk did not influence the absorption of flavour compounds by LLDPE. Because the fat present in skim milk was probably entrapped, only the proteins (especially casein) decreased the absorption of limonene and decanal. Whole milk, which contained a higher concentration of (free) fat, suppressed the absorption of all flavour compounds by LLDPE to the same extent as was found for the oil model solutions. In general, absorption results from skim milk and whole milk were in good agreement with the results of the investigated model solutions containing individual food components.

The composition of a food matrix showed to play a major role in the absorption of flavour compounds by LLDPE. The extent of flavour absorption by LLDPE is influenced by food components in the order: oil or fat >> polysaccharides and proteins > disaccharides.

E2MB

The absorption curves of E2MB followed a (strange) zigzag pattern during all 14 days of storage (Table 2.5 and 3.2). This pattern was not unique for one food component in particular, but all investigated food components showed similar E2MB absorption patterns, with the exception of the oil model solutions and whole milk. Up to a food component concentration of 10 g/l absorption of E2MB increased, which was probably due to a concentration or 'salting out' effect (loss of free water) of the more polar E2MB. At a food component concentration of approximately 15 g/l absorption of E2MB suddenly decreased. An explanation for this absorption 'drop' might be a rearrangement of the food matrix (i.e. Tween 80, food component and E2MB), resulting in a decrease of the amount of E2MB in the aqueous phase. However, static headspace analysis did not show a detectable decrease in the amount of free E2MB for all studied food components. Because other investigated flavour compounds were also not affected, it seems that this rearrangement of the food matrix is probably very small. At higher concentrations absorption of E2MB by LLDPE starts to increase again probably due to a 'salting out' effect.

Modelling

Many flavour absorption studies have dealt with determining the mass transport coefficients for organic vapours in polymer films. The transport of vapours is easier to evaluate mathematically than the transport of liquid sorbates, and the results can often be explained by absorption and diffusion theories. No foodstuffs, however, are present in the gaseous phase, and a more realistic approach is to study flavour absorption by polymers from liquids, either model solutions or actual liquid foods. However, the addition of an aqueous phase to the experimental system makes evaluation of the results more complex.[19] A determination of the relationship between flavour compounds and polymeric packaging materials for predicting flavour absorption would save research time for the packaging industry. Prediction of flavour absorption in relation to the packed food and the packaging material would be a valuable tool in product development. It can help the food industry in choosing packaging material or in determining product formulation.

In Chapter 4, a model based on the effect of the polarity (log P) of flavour compounds and on their partitioning coefficients between food(matrix) and packaging material is described. Results showed that the model fits nicely with experimental data. The model can be used for predicting absorption of flavour compounds from foods into LLDPE when lipids in the food matrix are the main factor in determining absorption of flavour compounds. However, in a

very low fat food matrix the model is not valid for compounds like aldehydes, which are able to interact strongly with proteins. Knowledge of solubility and binding behaviour of flavour compounds to non-volatile food components and their partitioning behaviour between different phases (component/water, component/oil or component/oil/water on one site and water/polymer, oil/polymer or water/oil/polymer on the other site) is of main importance to estimate the rate and amount of absorption from real food products by polymers. In the future, a fitting model could be extended with the dynamics of the absorption phenomena (including mass transfer effects as a consequence of product texture, viscosity, etc.) and also for different packaging materials.

8.3 Effect of storage time and temperature

Several investigations have shown that polyolefins (polyethylene and polypropylene) can absorb considerable amounts of flavour compounds. However, less information is available in literature about the influence of storage time and temperature on the amount of flavour absorption by polyesters, such as polyethylene terephthalate (PET), polycarbonaat (PC) and polyethylene naphthalate (PEN).

LLDPE, polypropylene (PP), PC, PET film, PET bottle and PEN were stored in a model solution containing 10 flavour compounds at 4, 20 and 40°C and flavour absorption by the plastic materials was followed in time (Chapter 5). Depending on storage temperature, the total amount of flavour absorption by the polyolefins was 3 to 2400 times higher than by the polyesters. Storage temperature, however, did not influence the total amount of flavour absorption by the rubbery polymers LLDPE and PP, while temperature raise did affect the rate of flavour absorption and quantity by the glassy polymers PC, PET and PEN. Rate and quantity of flavour absorption were related to differences in polymer characteristics (such as polarity, glass transition temperature and crystallinity) and to the structure and polarity of the different flavour compounds. From the point of view of flavour absorption (i.e. loss of flavour compounds), polyesters should be preferred over the polyolefins as packaging material.

8.4 Effect on oxygen permeability

The shelf-life of a food or beverage packaged in a polymer will depend on many factors. One of the most important factors is the rate at which oxygen from the air enters the package. Only a few papers reported that flavour absorption can affect the oxygen permeability of plastic packaging materials, and consequently the shelf-life of a food product, making it necessary to investigate this aspect more thoroughly.

In Chapter 6, the effects of flavour absorption on the oxygen permeability of low-density polyethylene (LDPE), PP, PC and PET were studied using an isostatic continuous flow system. Polymer samples were exposed to a model solution containing limonene, hexyl acetate, nonanone and decanal at 40°C. After exposure, one part of each sample was analysed for absorbed flavour compounds using Large Volume Injection GC Ultrasonic 'in vial' extraction. From the other part of the exposed sample the oxygen permeability was measured in a permeation cell at 25°C. After 8 hours of exposure, the oxygen permeability of the exposed LDPE and PP samples showed a significant linear increase of 21% and 130%, respectively. Owing to swelling of the polymer samples resulting from flavour absorption, the structure of the polymeric network changed (i.e. opened) and consequently increased oxygen permeability. Because of the higher oxygen permeability a reduction in the shelf-life of oxygen sensitive products, which are packed in LDPE or PP and contain the tested flavour compounds (such as orange juice and apple juice) can be expected.

The oxygen permeability of exposed PC samples, however, showed a significant linear decrease of 11% after 21 days of storage. PC obviously did not swell like LDPE or PP. Therefore, it was suggested that the absorbed flavour compounds occupied or blocked the 'micro-cavities' through which normally oxygen is transported. Flavour absorption will probably have a positive effect on the shelf-life of oxygen sensitive products packed in PC. Oxygen permeability of PET was not influenced by the presence of flavour compounds, meaning that PET remained a good oxygen barrier.

One should realise that the concentrations of flavour compounds in real food products are usually substantially lower than those used in this study, with the exception of limonene. Therefore, the observed oxygen permeability effect may be less or even not significant in foods and beverages.

8.5 Effect on taste perception

Knowledge of the impact of loss of flavour compounds by absorption into polymer packages on the sensory quality of foods is important for food and beverage manufacturers. In Chapter 7, the influence of flavour absorption by LDPE, PC and PET on taste perception of a model solution containing 7 flavour compounds and orange juice in glass bottles with and without (=control) pieces of the respective plastic films after dark storage at 20°C is described.

Due to flavour absorption by LDPE the concentration of flavour compounds in the model solution decreased substantially. From the model solution valencene was almost completely absorbed by LDPE, followed to a lesser extent by decanal, hexyl acetate, octanal and nonanone. Less flavour compounds were absorbed from the model solution by PC and PET. In contrast to LDPE, valencene was absorbed by PC and PET in the lowest amounts and decanal to the highest. Limonene was readily absorbed from orange juice by LDPE, while myrcene, valencene, pinene and decanal were absorbed in smaller quantities. From orange juice only three flavour compounds were absorbed in very small amounts by PC and PET: limonene, myrcene and decanal.

Although flavour content between controls and polymer treated samples differed substantially, the loss of flavour compounds due to absorption by LDPE, PC and PET did not influence taste perception of the model solution and orange juice significantly up to 29 days of dark storage at 20°C as determined by triangular taste panel tests. It is more likely that other mechanisms play a more important role, such as chemical degradation resulting in a development of off-flavour components. Therefore, storage temperature remains one of the most important factors in delaying flavour loss and achieving satisfactory shelf-life and quality.

8.6 Perspectives

The use of plastic packaging materials to replace glass and metal in food and beverage packaging is increasing every day. Nowadays, the quality of foodstuffs has more than ever included the notion that packaging contact is not always wholesome. It can alter the packaged food product by flavour absorption and can also affect the food by off-flavour release. Therefore, the search for superior barrier materials is underway at many chemical and

packaging companies. Opportunities in the packaging market are being created by the introduction of new high-barrier packaging materials, such as PEN, or multilayer polymers, such as EVOH + PET. Currently there have been indications that certain beer packaging users are seriously considering PEN as a possible material for beer bottles. The superior barrier properties of PEN might cause beer producers to consider PEN over other material choices, despite its higher costs. By using multilayer systems the specific properties of each individual polymer are combined and contribute to an excellent protection of the packed food. Absorption of flavour compounds by polymers is not necessarily a problem. Polyolefins are able to absorb substantial amounts of certain flavour compounds. Depending on the contribution of the absorbed flavour compounds to a food flavour the product quality might be affected. On the other hand polyesters absorb very low amounts of flavour compounds, which will not influence the product quality. If necessary, a multilayer system of polyolefins and polyesters may contribute positively in preventing an unbalance in flavour profile due to flavour absorption and keeping flavour compounds in the packed food.

Food technologists spend a considerable time in developing and producing food products with a desirable and delicate flavour balance. A possible change of flavour is one of the main factors which should be considered, because a good flavour is one of the first criteria for consumers to choose and buy certain food products. Therefore, attention to flavour-packaging interactions and their consequences is necessary to be sure that producers can guarantee the excellent quality of their food products.

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Samenvatting

In dit proefschrift zijn de volgende aspecten van aroma-absorptie door plastic verpakkingsmaterialen bestudeerd: de invloed van de levensmiddelenmatrix en de bewaarcondities (tijd en temperatuur), en het effect van absorptie op de zuurstofdoorlaatbaarheid van polymeren en de smaakgewaarwording van een product. In hoofdstuk 1 wordt het fenomeen aroma-absorptie ingeleid.

In hoofdstuk 2 en 3 wordt de invloed van eiwitten, koolhydraten en olie/vet op de absorptie van limoneen, decanal, linalool en ethyl-2-methylbutyraat (E2MB) door lineair low-density polyethyleen (LLDPE) beschreven. De invloed van eiwitten is onderzocht met een modelsysteem van β-lactoglobuline en caseïne, de invloed van koolhydraten met een modelsysteem van pectine, carboxymethylcellulose (CMC), lactose en saccharose en de invloed van olie met een modelsysteem van olie in water emulsies. Tevens is het effect van combinatiemodellen (olie/caseïne en olie/pectine) op de mate van aroma-absorptie onderzocht. De resultaten van de modelsystemen zijn vergeleken met twee commerciële producten, nl. magere en volle melk. β-lactoglobuline bleek decanal irreversibel te binden, waardoor na 14 dagen blootstelling de absorptie van decanal door LLDPE met meer dan 50% afnam. Caseïne bond limoneen en decanal hetgeen resulteerde in een afname van de absorptie met 40% en 90%. De aanwezigheid van CMC en pectine (verdikkingsmiddelen) zorgde ervoor dat de diffusie van limoneen en decanal van de levensmiddelenmatrix naar LLDPE trager verliep. Hierdoor nam de absorptiesnelheid van limoneen en, in minder mate, die van decanal af. Door een uitzoutingseffect van lactose en saccharose vond er een toename plaats van de absorptie van de minder apolaire aromacomponenten linalool en E2MB. De aanwezigheid van lactose, saccharose en CMC, daarentegen, verlaagde de absorptie van decanal door LLDPE na 14 dagen blootstelling. Deze afname werd waarschijnlijk veroorzaakt door een interactie tussen een suiker(residu) en decanal.

De invloed van olie op de mate van aroma-absorptie bleek aanzienlijk te zijn; door de aanwezigheid van een relatief kleine hoeveelheid olie (50 g/l) werd aroma-absorptie met ongeveer 90% verlaagd. Apolaire aromacomponenten lossen op in de oliefase en alleen de aromacomponenten opgelost in de waterfase zijn beschikbaar voor absorptie door LLDPE. De absorptie van het minder apolaire E2MB nam bij lage olieconcentraties eerst toe ten gevolge van een uitzoutingseffect, maar bij hogere olieconcentraties (> 2,5 g/l) nam de

absorptie weer af. De olie/caseïne en olie/pectine combinaties vertoonden een vergelijkbaar effect. De aanwezigheid van olie bleek een veel grotere invloed te hebben op de mate van aroma-absorptie dan de aanwezigheid van eiwitten en koolhydraten.

De absorptiewaarden vanuit magere en volle melk lagen in de lijn van de resultaten van de modelsystemen, hoewel het melkvet (1.11 g/l) in magere melk niet het verwachte effect had op de mate van aroma-absorptie. Waarschijnlijk is het aanwezige melkvet ingesloten en niet toegankelijk voor aromacomponenten, waardoor alleen de eiwitten absorptie-effecten voor hun rekening nemen. Volle melk, met een hogere concentratie aan (vrij) melkvet, zorgde voor eenzelfde mate van absorptieafname als de modelsystemen met olie. In het algemeen kwamen de resultaten van magere en volle melk goed overeen met de resultaten van de modelsystemen. De levensmiddelenmatrix bleek een grote rol te spelen bij de mate van absorptie van aromacomponenten door LLDPE. De mate van aroma-absorptie door LLDPE werd in de volgende volgorde beïnvloed: olie of vet >> polysacchariden en eiwitten > disacchariden.

Een model dat gebaseerd is op de polariteit (log P) van aromacomponenten en hun verdelingscoëfficiënt tussen de levensmiddelenmatrix en het verpakkingsmateriaal wordt beschreven in hoofdstuk 4. De resultaten laten zien dat het model goed overeenkomt met de absorptieresultaten zoals beschreven in hoofdstuk 2 en 3. Het model kan gebruikt worden om de mate van aroma-absorptie door LLDPE te voorspellen bij levensmiddelen, waarin olie/vet de bepalende factor voor absorptie is. Bij producten met een zeer laag vetgehalte en bij aromacomponenten die in staat zijn interacties aan te gaan met eiwitten, zoals aldehydes, kent het model beperkingen.

Verschillende onderzoeken hebben aangetoond dat de polyolefins, zoals polyethyleen (PE) en polypropyleen (PP), grote hoeveelheden aromacomponenten kunnen absorberen. Minder informatie is echter beschikbaar over de invloed van bewaartijd en -temperatuur op de mate van aroma-absorptie door polyesters, zoals polyethyleen terephthalaat (PET), polycarbonaat (PC) en polyethyleen naphthalaat (PEN). In hoofdstuk 5 is een onderzoek beschreven waarbij LLDPE, PP, PC, PET film, PET fles en PEN is blootgesteld gedurende een bepaalde tijd bij 4, 20 en 40ºC aan een modeloplossing met 10 verschillende aromacomponenten. De totale hoeveelheid aroma die geabsorbeerd werd door de polyolefins was, afhankelijk van de bewaartemperatuur, 3 tot 2400 keer hoger dan bij de polyesters. De bewaartemperatuur had echter geen invloed op de totale hoeveelheid absorptie door de ‘rubberachtige’ polymeren (LLDPE en PP). Stijging van de temperatuur had echter wel een effect op de absorptiesnelheid en -hoeveelheid van de ‘glasachtige’ polymeren (PET, PC en PEN).

Absorptiesnelheid en -hoeveelheid bleken af te hangen van de polymeereigenschappen (zoals polariteit, glastransitietemperatuur en kristalliniteit) alsmede van de structuur en polariteit van de verschillende aromacomponenten. Aangezien de mate van absorptie groter is door polyolefins, vergeleken met polyesters, verdient het gebruik van polesters de voorkeur uit het oogpunt van aroma-absorptie.

De houdbaarheid van een in een polymeer verpakt product hangt af van veel factoren. Een van de meest belangrijke factoren is de snelheid waarmee zuurstof uit de lucht een verpakking binnendringt. In hoofdstuk 6 is het effect van aroma-absorptie op de zuurstofdoorlaatbaarheid van low-density polyethyleen (LDPE), PP, PC en PET beschreven. Gedurende een bepaalde periode zijn de polymere monsters bij 40ºC blootgesteld aan een modeloplossing die een mengsel bevatte van limoneen, hexylacetaat, nonanon en decanal.

Na blootstelling werd een deel van elk monster geanalyseerd op de hoeveelheid geabsorbeerde aromacomponenten. Van het andere deel van het monster werd de zuurstofdoorlaatbaarheid bepaald m.b.v. een ‘isostatic continuous flow’ systeem bij 25ºC. Na 8 uur blootstelling steeg de zuurstofdoorlaatbaarheid van LDPE en PP significant lineair met 21% en 130%. Deze stijging werd veroorzaakt door het opzwellen van de polymeren ten gevolge van aroma-absorptie waardoor de structuur van het polymere netwerk veranderde (openging). Zuurstofgevoelige producten die verpakt zijn in LDPE of PP en die de onderzochte aromacomponenten bevatten (zoals sinaasappelsap en appelsap) kunnen door de hogere zuurstofdoorlaatbaarheid t.g.v. aroma-absorptie korter houdbaar zijn.

De zuurstofdoorlaatbaarheid van PC vertoonde daarentegen na 21 dagen blootstelling een significant lineaire daling van 11%. PC zwelde kennelijk niet zo op als LDPE of PP. Waarschijnlijk bezetten of blokkeerden de geabsorbeerde aromacomponenten de ‘micro-cavities’ waardoor normaliter zuurstof wordt getransporteerd. Aroma-absorptie zal daarom een positief effect hebben op de houdbaarheid van in PC verpakte producten. Aroma absorptie bleek geen invloed te hebben op de zuurstofdoorlaatbaarheid van PET. Men moet zich echter realiseren dat de aromaconcentraties in levensmiddelen lager zijn, met uitzondering van limoneen, dan de concentraties gebruikt in dit onderzoek. De waargenomen zuurstofdoorlaatbaarheidseffecten worden daarmee enigzins gerelativeerd.

Kennis over de invloed die het verlies van aromacomponenten door aroma-absorptie in plastic verpakkingen heeft op de sensorische kwaliteit van een product is zeer waardevol voor levensmiddelenfabrikanten. In hoofdstuk 7 wordt de invloed beschreven van aroma-absorptie door LDPE, PC en PET op de smaakgewaarwording van een modeloplossing met 7 aromacomponenten en sinaasappelsap. Gedurende 29 dagen zijn de modeloplossing en het

sinaasappelsap in glazen flessen bewaard in het donker bij 20ºC en al dan niet (= blanco) blootgesteld aan de verschillende plastic monsters. De concentratie aromacomponenten in de modeloplossing daalde aanzienlijk als gevolg van absorptie door LDPE. Valenceen in de modeloplossing werd bijna volledig geabsorbeerd door LDPE, in mindere mate gevolgd door decanal, hexylacetaat, octanal en nonanon. PC en PET absorbeerden minder aromacomponenten. In tegenstelling tot LDPE, werd valenceen het minst en decanal het meest door PC en PET geabsorbeerd.

Limoneen werd vrij gemakkelijk uit sinaasappelsap geabsorbeerd door LDPE, terwijl myrceen, valenceen, pineen en decanal in veel lagere hoeveelheden werden geabsorbeerd. PC en PET waren slechts in staat om drie aromcomponenten in zeer lage hoeveelheden uit sinaasappelsap te absorberen, namelijk limoneen, myrceen en decanal. Hoewel de gehaltes aan aromacomponenten tussen de al dan niet aan de polymeren blootgestelde modeloplossing en het sinaasappelsap aanzienlijk verschilden, was geen significant effect waarneembaar in de smaakgewaarwording. Het is waarschijnlijker dat verandering in smaakgewaarwording veroorzaakt worden door andere mechanismen, zoals de vorming van off-flavour componenten door chemische degradatie. De bewaartemperatuur blijft daarom een van de belangrijkste factoren om aromaverlies te vertragen en om een bevredigende houdbaarheid en kwaliteit van levensmiddelen te bewerkstelligen.

Nawoord

De wens om te promoveren ontstond in 1993 toen ik tijdens mijn afstudeerperiode een promotie bijwoonde. Het idee om vier jaar onderzoek te doen op een interessant onderwerp sprak mij toen ontzettend aan. Ik heb dan ook meteen JA gezegd, toen Jozef Linssen mij in 1996 vroeg of ik als AIO onderzoek wilde doen naar de effecten van aroma-absorptie door verpakkingsmaterialen. Nu, zes jaar later, moet ik bekennen dat ik blij ben dat het eindelijk af is. Een aantal keren heb ik overwogen om er de brui aan te geven, en mezelf afgevraagd of het allemaal wel de moeite waard was. Terugkijkend, kan ik gelukkig constateren dat ik niet alleen veel onderzoekservaring heb opgedaan, maar vooral dat ik veel over mezelf en mijn capaciteiten heb geleerd.

Het schrijven van een nawoord is eigenlijk het leukste deel van een proefschrift. Niet alleen omdat het einde in zicht is, maar vooral omdat ik eindelijk alle mensen mag bedanken die mij daarbij geholpen hebben.

Jozef, jou wil ik als co-promotor als eerste bedanken voor alle begeleiding. Ik kon altijd bij je aankloppen voor vragen en je nam alle tijd om ze te beantwoorden. Vooral de urenlange discussies over artikelen of commentaren van reviewers heb ik zeer gewaardeerd. Gelukkig heb je mijn drang naar perfectionisme regelmatig weten te temperen, want anders had het nog langer geduurd. Jan Cozijnsen, bedankt voor de introductie in de wereld van de gaschromatografie en alle ondersteuning die je me hebt gegeven. Een gaschromatograaf is voor mij geen ‘black box’ meer. Ik heb grote bewondering voor het feit dat je vaak je eigen werk meteen neerlegde om mij of andere mensen te woord te staan of te helpen. Ik ben er trots op om jou als paranimf naast me te hebben staan. Fons Voragen, bedankt voor het lezen van alle artikelen en je objectieve commentaar hierop. Het was fijn om een promotor te hebben die wat verder van mijn onderzoek afstond en de grote lijnen in de gaten hield.

Els van den Heuvel, Marisa Navarro y Koren, Diane Schoolmeester en Annelieke van Ooij, veel resultaten in dit proefschrift heb ik aan jullie te danken. Bladerend door het proefschrift zal het voor jullie één grote herkenning zijn. Vooral jullie gedrevenheid heeft mijn motivatie tijdens het promotieonderzoek versterkt.

Aagje Legger, bedankt voor alle hulp en ondersteuning bij het sensorisch onderzoek. Door jouw enthousiasme ben ik sensorisch onderzoek een stuk interessanter gaan vinden. Kees Wisse, bedankt voor je hulp en de levering van de monsters voor het sensorisch onderzoek.

Henk van der Stege en Marcel Meinders wil ik bedanken voor alle ondersteuning bij het tot standkomen van hoofdstuk 6. Henk, jouw hulp bij de ontwikkeling van de zuurstofpermeatie-opstelling was zeer belangrijk. Marcel, veel tijd heb je me bespaard met het door jouw geschreven computerprogramma. Matthijs Dekker wil ik bedanken voor zijn essentiële bijdrage aan hoofdstuk 4 en Katja Grolle voor de hulp bij de viscositeitsmetingen.

Harold Bult, van alle mensen op de vakgroep had ik toch het meeste contact met jou. Niet alleen omdat we allebei onderzoek deden op het gebied van aroma's, maar ook omdat het goed klikte tussen ons. Zonder jouw kracht en inzet waren we trouwens nooit zover gekomen bij drie edities van het Oranje-Groen Roeitoernooi. Ik ben bijzonder blij dat je mijn paranimf wilt zijn.

Ik wil alle mede AIO's en vakgroepgenoten bedanken voor alle ondersteuning en de ontzettend leuke tijd op de vakgroep en bij het mensahappen. Alle panelleden die hebben deelgenomen aan het sensorisch onderzoek bedankt dat jullie de soms vieze drankjes hebben willen proeven. Alle familie, vrienden, kennissen en collega's, bedankt voor de interesse die jullie hebben getoond in mijn promotieonderzoek.

Lieve pap en mam, dit proefschrift heb ik aan jullie opgedragen omdat jullie mij altijd gestimuleerd hebben. Zonder jullie onvoorwaardelijke steun zou dit proefschrift nooit tot stand zijn gekomen. Van jullie heb ik doorzettingsvermogen gekregen en de wil om het beste uit mezelf te halen. Esmee, lieve zus, bedankt voor je steun en interesse. Mireille, hoewel je pas bij de afronding van het proefschrift in mijn leven kwam, was je toch zeer belangrijk. Niet alleen heb je me gestimuleerd, maar je hebt ook zeer veel geduld gehad toen ik avonden achtereen zat te schrijven. Ik hou van jullie!

Remco

Curriculum Vitae

Remco Willem Godefridus van Willige werd op 20 mei 1971 geboren te Nuth. In 1989 behaalde hij het Gymnasium diploma aan het Gymnasium Rolduc te Kerkrade. In datzelfde jaar startte hij met de studie Levensmiddelentechnologie aan de Landbouwuniversiteit te Wageningen (LU). In juni 1995 studeerde hij af met afstudeervakken in de Levensmiddelenchemie en Kwaliteitsborging en met een stage bij het Dairy Product Centre in Fermoy, Ierland. Van juni 1995 tot augustus 1996 was hij werkzaam in het chemicaliënmagazijn van de LU. Vervolgens werkte hij van augustus 1996 tot september 2000 als Assistent in Opleiding bij de leerstoelgroep Levensmiddelenchemie van het Departement Agrotechnologie en Voedingswetenschappen aan de LU. Het onderzoek uitgevoerd in deze periode wordt beschreven in dit proefschrift. Vanaf april 2001 is hij werkzaam als Projectleider bij de afdeling Papier en Karton van TNO Industrie te Delft.

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