



THE SWEDISH INSTITUTE FOR FOOD AND BIOTECHNOLOGY

# Active food packaging -Materials and interactions

a literature review

Anna Svensson

This review is a part of a PhD work at the Department of Chemical Engineering,  
Karlstad University, Karlstad, Sweden.

Supervisors: Anders Leufvén (SIK) and Lars Järnström (KaU)  
Göteborg 2004

SIK-report 2004 No.727

SIK-report 2004 No.727

# Active food packaging

## -Materials and interactions

a literature review

Anna Svensson

This review is a part of a PhD work at the Department of Chemical Engineering,  
Karlstad University, Karlstad, Sweden.

Supervisors: Anders Leufvén (SIK) and Lars Järnström (KaU)

SIK, The Swedish Institute for Food and Biotechnology  
Göteborg 2004

ISBN: 91-7290-235-3

<b>1. Introduction .....</b>	<b>1</b>
<b>2. Food packaging .....</b>	<b>2</b>
2.1. The need of packaging .....	2
2.2. Materials in food packaging .....	2
2.2.1. Polyethylene .....	2
2.2.2. Polypropylene .....	3
2.2.4. Polystyrene .....	3
2.2.3. Polyethylene terephthalate .....	3
2.2.5. Polyamide .....	3
2.2.6. Ethylene vinyl alcohol .....	4
2.3. Driving forces for new concepts in packaging .....	4
2.4. Active packaging .....	4
2.4.1. Oxygen scavengers .....	6
2.4.2. Ethylene absorbers and emitters .....	6
2.4.3. Moisture control .....	7
2.4.4. Carbon dioxide absorbers and emitters .....	7
2.4.5. Odour removers .....	8
2.4.7. Antimicrobial agents .....	9
2.4.8. Aroma release .....	10
2.4.9. Modified atmosphere packaging .....	11
2.5. Intelligent packaging .....	12
<b>3. Food and packaging interactions .....</b>	<b>13</b>
3.1. Permeation, migration and sorption .....	13
3.2. Laws of diffusion and solubility .....	14
3.3. Parameters affecting the degree of food flavour - packaging interactions .....	16
3.4. Undesirable effects of food packaging interactions .....	18
3.5. Desirable effects of food packaging interactions .....	18
<b>4. Deteriorative reactions in foods .....</b>	<b>19</b>
4.1. Enzymatic reactions .....	19
4.2. Chemical reactions .....	19
4.3. Physical changes .....	21
4.4. Biological changes .....	21
<b>5. Odour release from paper and plastic .....</b>	<b>23</b>
<b>6. Legislation .....</b>	<b>24</b>
6.1. Directives applicable to all food contact materials and articles .....	24
6.2. Directive for plastic food contact materials .....	25
6.3. Regulations for active and intelligent packaging .....	26
<b>7. Latex coating –an alternative to customary plastic materials .....</b>	<b>28</b>
7.1. Latex synthesis .....	28
7.2. Film formation .....	29
7.3. Types of latexes .....	30
7.4. Latex binders for pigment coating .....	31
7.5. Barrier dispersion coatings .....	31
7.6. Surface sizing .....	32
<b>8. Recycling of packaging materials .....</b>	<b>33</b>
<b>9. References .....</b>	<b>35</b>

## **1. Introduction**

This literature review is a part of a PhD-project entitled “Active product packaging interactive surfaces”. The project is a collaboration between Sensory and Flavour Evaluation at SIK (The Swedish Institute for Food and Biotechnology) in Göteborg, Sweden and the Surface Treatment Programme at Karlstad University in Karlstad, Sweden.

In this review, conventional and new food packaging materials are presented as well as new developments in food packaging techniques i.e. active and intelligent packaging. Interactions between the food product and the packaging material are described including how these interactions can be used in a positive way to affect food quality. The review also contains sections describing how food products are deteriorated and how packaging materials are recycled. In addition description of water based coatings for paper and board are included. Further, the European legislation for food contact materials and the EU-sponsored project Actipak are presented.

The literature search was performed during the period of October 2003 until February 2004. (However, some parts about legislation have been added later, during October 2004.) The literature covered in this review encompasses papers and books, but also some patents. Data bases used include FSTA (Food Science and Technology Abstracts), Science Direct, Paperbase and SciFinder as well as the national library catalogue Libris plus the internet site Espacenet for patent information.

## 2. Food packaging

### 2.1. *The need of packaging*

An efficient food packaging provides several functions. It serves as a container to hold and carry the food product as well as a protection of the food from outside contamination by water, light, odours, microorganisms, dust etc and from mechanical damage, thereby preserving the food quality. The package may also provide barriers to maintain correct moisture content or gas composition around the product. In addition, convenience is important in packaging and the demands for easy opening, dispensing and resealing packages, which retain the quality of the product until totally used, are increasing. The food package must also be communicative to facilitate trading as well as to promote sales and inform about content and nutritional properties (Paine and Paine 1992; Risch 2000; Robertson 1993).

### 2.2. *Materials in food packaging*

The most commonly used materials in food packaging include paper, plastic, metal and glass (Paine and Paine 1992). Glass and metal have excellent barrier properties and hardly interact with the packaged food at all. Plastic materials demonstrate almost the opposite properties including non-ideal barriers and non-inertness resulting in interactions with food products (Nielsen and Jaegerstad 1994). For example aroma compounds may be absorbed in the plastic material resulting in loss in aroma intensity or an the unbalanced flavour profile (van Willige *et al.* 2002). Nevertheless, the use of plastic materials in packaging has increased rapidly during the last decades. The main reasons for this are that plastics are less expensive than other materials, they have lower energy content and lighter weight but are still relatively strong. Further, there are several types of plastic materials resulting in many alternatives in forming and shaping plastic products and a diversity in possible applications (Paine and Paine 1992).

In many cases different materials are combined to get the desired barrier properties of the package. The layers may include foil, different kinds of plastic, paper and adhesives. The most important plastics in food and drink packaging are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyamide (PA) and ethylene vinyl alcohol (EVOH) (Crosby 1981; Dunn 1997; Risch 2000). PE is the most commonly produced plastic in the world and PP is the third most common bulk plastic after polyvinyl chloride (PVC) (Piringer and Baner 2000).

#### 2.2.1. *Polyethylene*

There are several grades of polyethylene and the three main types are low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) among which LDPE is most frequent in packaging. The mechanical properties of PE depend on the molecular weight and degree of branching. The most important properties of PE in packaging applications include its heat sealability, toughness, high elasticity, cold resistance and good water vapour resistance. LDPE, which is highly branched, is flexible and can be manufactured into films, bottles, closures, dispensers, coatings on paper or aluminium foil as well as to large tanks and containers. The permeability of gases, aromas and fats are high for LDPE resulting in that LDPE must be combined with other materials in some food packaging applications. For example, solely LDPE is not suitable for applications where oxidation is a problem. With increasing density the crystallinity increases and therefore

barrier properties as well as hardness and stiffness of PE increase while toughness, cold resistance and transparency decrease. LLDPE is generally stronger and tougher than LDPE but has similar properties. HDPE is harder and more brittle than LDPE and has better barrier properties. HDPE is used as storage and distribution containers but also as films with high fat resistance for meat and other products (Crosby 1981; Paine and Paine 1992; Piringer and Baner 2000; Robertson 1993).

### ***2.2.2. Polypropylene***

PP has similar chemical composition as PE but it is harder and has a less waxy feel. It is produced as films, sheets, trays and bottles which maintain their shapes at high temperatures. As a result they can be hot-filled or sterilized. PP has great grease and solvent resistance. Other characteristic properties of PP are its resistance to fatigue when flexed and that it does not undergo stress cracking. However PP has low cold temperature resistance. Biaxially oriented films of PP has improved gloss, clarity, impact strength and water and oxygen barrier properties They are used for wrapping of several food items including snack foods and biscuits (Crosby 1981; Paine and Paine 1992; Piringer and Baner 2000).

### ***2.2.4. Polystyrene***

PS is hard, transparent and has good water resistance (Strong 2000). The main drawback is its brittleness and sensitivity to stress cracking and high gas and moisture vapour permeability. Due to the latter property the main applications of PS are to products with short shelf lives like yoghurt, ice cream, fresh cheese and coffee cream. However, in the past few years PS has been replaced by the less expensive PP (Paine and Paine 1992; Piringer and Baner 2000; Strong 2000).

### ***2.2.3. Polyethylene terephthalate***

The polyester PET has great tensile strength (it must be orientated to develop full tensile strength), excellent chemical resistance, light weight, elasticity and good temperature stability. Due to the good temperature stability PET products like boil-in-the-bag or oven bags have been produced. The barrier properties of gases, aromas and fats are good for PET while the water vapour permeability is a bit higher. Biaxially stretched PET, which is stronger and has better gas barrier than unstretched PET, is used in containers for carbonated beverages, edible oils and spirits. To improve sealability and toughness of PET coatings of LDPE can be made (Paine and Paine 1992; Piringer and Baner 2000). Also metallization (Piringer and Baner 2000), silica coating, epoxy amine coating and polyvinylidene chloride coating (Braakman 2002) of PET leads to improvement of barrier properties.

### ***2.2.5. Polyamide***

There is a large variety of polyamides, commonly called nylons. Since hydrogen bonds are formed between the molecules, PA is hard, temperature resistant and some types have high crystallinity. The melting point of PA is between 177-255°C and it can be used at low temperatures ranging from -50°C to -70°C. Further, PA is a good gas barrier while the barrier properties to water are not so good. However, PA is rather expensive and the main application is in laminates with for example PE. PE gives good water resistance and heat sealability. These laminates are for example used for vacuum or inert gas packed meat products, fish and cheeses. Biaxial stretching of PA improves stiffness of the material and is used as carrier film in laminate packages for stiffer vacuum or inert gas packing of coffee, milk powder and meat

products as well as for “bag-in-box” liquid packages (Paine and Paine 1992; Piringer and Baner 2000).

#### **2.2.6. Ethylene vinyl alcohol**

EVOH is a plastic with exceptional barrier properties which is manufactured by saponification of the ethylene vinyl acetate copolymer (EVA) (Piringer and Baner 2000). Under dry conditions EVOH has excellent oxygen barrier properties but is inherently moisture sensitive and becomes permeable when absorbing moisture. This is a big problem during sterilization and EVOH is therefore used as barrier material in multilayer constructions with for example PE. (Rowan 2001; Tsai and Wachtel 1990) EVOH has also been an excellent flavour barrier in contrast to other plastic materials, which may scalp desirable aromas from the food product. Therefore EVOH is also used as a barrier against flavour loss (Brody 1992).

### **2.3. Driving forces for new concepts in packaging**

New developments in food packaging are underway and the main driving forces for these changes include consumer demands, industrial competition and regulatory aspects (Dennis 2000). Environmental concern and efforts to decrease the solid waste stream are crucial. The requirements from the consumers include mildly preserved, high quality convenience food as well as greater assurance of food safety and better information of the food product (Franke *et al.* 2002; Risch 2000).

The globalization of the food industry demands products with longer shelf life and lighter weight materials. To address these needs, research is ongoing to improve barrier properties of the packaging as well as develop new concepts such as active and intelligent packaging. Barrier properties of the package has been improved by combining different materials as foil, different kinds of plastic, paper and adhesives through lamination, coextrusion or coating (de Kruijf *et al.* 2002; Franke *et al.* 2002; Risch 2000).

### **2.4. Active packaging**

New packaging concepts have been and are currently developed that not just function as a passive, inert barrier to external conditions but play an active role in the protection of the packed food (Anon 2002; Vermeiren *et al.* 2002). According to de Kruijf *et al.* (2002) active packaging can be defined as a package that changes the condition of the packaged food to extend shelf life or improve food safety or sensory properties, while maintaining the quality of the packed food (de Kruijf *et al.* 2002).

Shelf life and quality of the packed food may be improved or preserved by controlling appropriate conditions within the package. These conditions include physiological processes such as respiration of fresh fruits and vegetables, chemical processes such as lipid oxidation, physical processes like staling of bread and dehydration and also microbiological aspects as spoilage from microorganisms (de Kruijf *et al.* 2002).

As presented in table 1, examples of active packaging techniques include systems that absorb oxygen, ethylene, moisture, carbon dioxide and odours as well as systems that release carbon dioxide, ethanol, antimicrobial agents, antioxidants and flavours (Ahvenainen and Hurme

1997; Brody 2003; de Kruijf *et al.* 2002; Floros *et al.* 2000; Labuza 1996; Lopez-Cervantes *et al.* 2003; Vermeiren *et al.* 2002; Vermeiren *et al.* 1999). Often the active function is incorporated in separate units like sachets, pouches, labels etc instead of being integrated within the packaging material. The first application was desiccants in dry product packages (Brody *et al.* 2001).

Several active and intelligent packaging concepts are currently available on the market in USA, Japan and Australia. Until today only a few of these technologies are applied in Europe due to strict regulations in the legislation for materials intended to come in contact with food. Work is however ongoing to make amendments in the EU law in order to accept some types of active packaging. Also considerations of consumer acceptance, economic aspects, environmental impact and the effectiveness of the new concepts are lacking to some extent (de Kruijf *et al.* 2002). (See chapter 6, Legislation)

**Table 1.** Examples of active and intelligent packaging systems (Ahvenainen 2003; Ahvenainen and Hurme 1997; Brodie and Visioli 1992; Brody *et al.* 2001; Floros *et al.* 2000; Hurme *et al.* 2002; Rooney 1997; Vermeiren *et al.* 1999).

System	Form	Reagent	Function	Application
<b>O<sub>2</sub>-absorbent</b>	Sachet, label, cap or film	Ferrous compounds Metallic salts Organometallic compounds Pd/Pt catalysis Glucose oxide / Ethanol oxide	Inhibit lipid oxidation, mould growth, discolouration	Fats, oils, nuts bakery products, roasted coffee, meat, cheese, dried fruit, beverages etc.
<b>CO<sub>2</sub>-absorbent</b>	Sachet or film	CaOH + NaOH or KOH	Adsorb produced CO <sub>2</sub> to prevent swelling of the package	Roasted coffee and cheese
<b>Ethylene-absorbent</b>	Sachet or film	Aluminium oxide + potassium permanganate Chrystobalite Activated carbon Zeolite	Control ripening of fruits and vegetables	Fruit and vegetables
<b>Odour-absorbent</b>	Film	Polyethylene imine  Ascorbic acid and iron salt (ferrous sulphate) dispersed in plastic	Preserve smell and taste Remove off-odours	Adsorb aldehydes from oxidation of fats and oils Remove amine or sulphur-compounds from fish in domestic refrigerators
<b>Moisture-adsorbent</b>	Sachet or film	Glycerol Polyvinyl alcohol Clay Silica gel	Control moisture content	Dry foods, meat and vegetables
<b>Antimicrobial</b>	Sachet or film	Nisin Chitosan Horradish derivative Ceramic compounds (e.g. silver zeolite and zinc oxide)	Prevent microbial growth	Fish, fresh fruits, cheese, meat, bread
<b>Antioxidants</b>	Film	BHT BHA Vitamin C or E	Prevent lipid oxidation	Cereals, wine
<b>CO<sub>2</sub>-emitters</b>		Ascorbic acid Ferrous carbonate+metal halide	Control ripening of vegetables	Vegetables
<b>Ethanol-emitters</b>	Sachet	Ethanol adsorbed in silica powder (release ethanol in response to water adsorption)	Prevent microbial growth and staling	Bakery products and semi-dry fish
<b>Time-temperature-indicators (TTI)</b>	External label	Mechanical Chemical Enzymatic	Show temperature exposure	Frozen products, dairy products, fresh fruit and vegetables
<b>O<sub>2</sub>-indicators</b>	Internal label	Redox dyes or pH dyes	Show O <sub>2</sub> -content in MAP	Food stored in packages with reduced O <sub>2</sub> conc.
<b>Temperature-control</b>	Microwavable Self-heating Self-cooling	Reduce heating by foil shields or crisp or brown some components Exothermic reactions (lime with water) Endothermic reactions (ammonium nitrate or ammonium chloride with water)	Heat or cool the product	Popcorn, pizza, beverages and ready-to-eat-meals

### **2.4.1. Oxygen scavengers**

The most common type of active package today is oxygen removers. Oxygen present in food packages can deteriorate many types of foods, especially food items containing lipids e.g. bread, biscuits, pizzas, cured or smoked meat and fish, cheese, nuts, chocolate but also products like coffee or tea (Lopez-Cervantes *et al.* 2003). Removal of oxygen can preserve the food quality by decreasing food spoiling reactions, reducing oxidative rancidity, inhibit oxidation of pigments and vitamins, control enzymatic discolouration and inhibit growth of aerobic microorganisms (Brody *et al.* 2001; Hotchkiss 1995; Labuza 1996). There are different ways to remove oxygen or prevent it from entering the interior of the package. Antioxidants, absorbers and scavengers are used (Brody *et al.* 2001; Smith *et al.* 1995). The definitions used for these techniques may however overlap.

Antioxidants are oxidized by radicals from lipids or peroxides or in light with single oxygen resulting in consumption of oxygen. These antioxidants are often blended with the food and not incorporated in the packaging material. Commonly used antioxidants are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and propyl gallate. Other antioxidants include vitamin A,  $\beta$ -carotene,  $\alpha$ -tocopherol (i.e. vitamin E) and ascorbic acid. The BHA/BHT compounds are also often incorporated into plastic films to retard oxidation of the plastic materials. Further applications are incorporation of antioxidants into the packaging material for diffusion to the interior of the package and transfer to the food product. (Brody *et al.* 2001; Wessling *et al.* 1999).

Oxygen scavengers are incorporated into the package structure or in sachets and remove oxygen by chemical reactions. The most widely used oxygen scavengers are ferrous compounds (Ahvenainen 2003; Brody *et al.* 2001; Lopez-Cervantes *et al.* 2003; Smith *et al.* 1995; Wakabayashi *et al.* 1992; Vermeiren *et al.* 2003). Further oxygen scavengers include catechol (Brody *et al.* 2001), ascorbic acid (Brody *et al.* 2001; Lopez-Cervantes *et al.* 2003; Smith *et al.* 1995), oxidative enzymes such as glucose oxidase (Ahvenainen 2003; Vermeiren *et al.* 2003), unsaturated hydrocarbons (Vermeiren *et al.* 2003) and polyamides (Brody *et al.* 2001).

Oxygen absorbers trap oxygen physically and not through chemical reaction. There are however very few materials that may be able to remove oxygen physically. Therefore the term oxygen absorber is often used to describe any system that somehow removes oxygen in a routine manner (Brody *et al.* 2001).

### **2.4.2. Ethylene absorbers and emitters**

Ethylene is a plant hormone produced during the energy generation processes in living cells of some fruits. These fruits, which are called climacteric, include apples, avocados, bananas, mangos, pears, kiwis and tomatoes. Non-climacteric fruits include grapes, lemons, oranges, pineapples and strawberries (Brody *et al.* 2001; Fennema 1996).

It has been known for long that even low concentrations of ethylene accelerate ripening of all fruits and vegetables, both climacteric and non-climacteric by stimulating the respiration rate. For example ethylene is used commercially to ripen bananas and tomatoes as well as to get orange colour on the oranges. By removing ethylene from the surrounding environment of the fruit or vegetable, the respiration rate is slowed resulting in slower ripening and therefore longer shelf life (Fennema 1996; Vermeiren *et al.* 2003; Zagory 1995).

The most common way to remove ethylene is by its reaction with potassium permanganate (KMnO<sub>4</sub>). When potassium permanganate oxidises ethylene to ethylene glycol, its colour changes from purple to brown. This concept is used in the form of sachets in individual boxes while blankets and tubes impregnated with KMnO<sub>4</sub> are utilized in transport vehicles (Brody *et al.* 2001; Zagory 1995).

Other ethylene removers include activated charcoal (Brody *et al.* 2001; Zagory 1995), bentonite (Brody *et al.* 2001) and aluminosilicates i.e. zeolites (Brody *et al.* 2001). In Korea, an ethylene scavenger called Orega has been developed that is composed of a film of fine porous containing minerals such as zeolite, active carbon, cristobalite and clinoptilolite (Brody *et al.* 2001; Zagory 1995). In Austria the ethylene absorber “ProFresh” containing an non-identified mineral based scavenger has been produced and is utilized commercially in several countries (Brody *et al.* 2001). This product has also shown capacity to adsorb some odours. Dunapak in Hungary has developed a paper called Frisspack containing silica gel that adsorbs ethylene combined with KMnO<sub>4</sub>-particles that oxidise ethylene. However, to adsorb ethylene effectively large amounts of silica gel is required (Brody *et al.* 2001; Zagory 1995).

#### **2.4.3. Moisture control**

Water is produced in respiring foods during the metabolism of fats and carbohydrates and wet food give high water vapour pressure (Labuza 1996). Condensation is therefore common in many packed foods especially for fruits and vegetables. When there is a temperature difference within or outside the package, water droplets appear on the packaging walls or cover the food surface. Water droplets on the packaging surface results in worsen package appearance as well as less consumption, while a moisten food surface results in increased surface mould growth and therefore diminished shelf life of the food product. This can be avoided by using a desiccating film or sachet (Brody *et al.* 2001; Hurme *et al.* 2002; Powers and Calvo 2003; Rooney 1997).

Pads filled with propylene glycol or cellulose fibre pads are often used in contact with meat and fish within the packages in order to adsorb water (Hurme *et al.* 2002; Labuza 1996). For dry foods the most commonly used desiccants are silica gels, which can adsorb up to 35% of their own weight in water (Brody *et al.* 2001; Powers and Calvo 2003). Other desiccants include salts such as sodium chloride (Brody *et al.* 2001; Hurme *et al.* 2002), glucose solutions encapsulated between water vapour permeable films (not water permeable) (Brody *et al.* 2001), and water adsorptive polymers (Hurme *et al.* 2002) like sodium polyacrylate as well as zeolites. Currently most work is focused on finding better solutions to incorporate the desiccant within the packaging (Brody *et al.* 2001; Hurme *et al.* 2002; Labuza 1996).

#### **2.4.4. Carbon dioxide absorbers and emitters**

High levels of carbon dioxide within the package have antimicrobial effects on the surface of some foods such as meat and poultry resulting in longer storage life. However since carbon dioxide is more permeable through plastics than oxygen, generation of carbon dioxide in the packaging may be necessary to keep the desired gas composition in some cases. (Matche 2001; Vermeiren *et al.* 1999).

Carbon dioxide adsorption is also utilized to prevent pressure built up, swelling and even bursting of the package of respiring foods resulting in decreased shelf life of the products. There has been much work done to minimize pressure built up in kimchi packages. (Kimchi, which are fermented vegetables like cabbage and onion and which are very popular in Korea,

produce carbon dioxide when packed even at cold storage.) Zeolite has been shown to adsorb carbon dioxide effectively resulting in reduced swelling of the packaging of kimchi (Lee *et al.* 2001).

In roasted coffee, there is lots of carbon dioxide present due to Strecker degradation reaction between sugars and amino acids (Floros *et al.* 2000; Vermeiren *et al.* 1999). A scavenger with a mixture of iron powder and CaOH reduces both the oxygen- and the carbon dioxide-levels. The lower carbon dioxide content results in prevention of bursting of the packaging and the lower oxygen content results in less oxidative flavour changes. Consequently, the shelf life will be extended (Floros *et al.* 2000; Labuza 1996; Smith *et al.* 1995; Vermeiren *et al.* 1999).

It is desirable to use carbon dioxide generators to avoid collapse of packages containing oxygen-scavengers. These systems are mostly based on ferrous carbonate or a mixture of ascorbic acid and bicarbonate. The main applications for systems combining oxygen-absorbers and carbon dioxide emitters are for products where packaging volume and package appearance are crucial such as for peanuts and potato crisps (Rooney 1995; Smith *et al.* 1995).

#### **2.4.5. Odour removers**

Further examples of active packaging concepts include removal of unpleasant aromas and flavours. Applications for scavengers of undesirable odours include removal of amines, which are produced under oxidation of protein-rich foods like fish, removal of aldehydes produced by oxidation of fatty acids in biscuits, fried foods and cereals as well as removal of bitter tasting components like limonin in fruit juices. (Brody *et al.* 2001; de Kruijf *et al.* 2002; Hotchkiss 1995; Rooney 1997; Vermeiren *et al.* 2003) Plenty of work on odour removal by porous pads has been done with products like diapers but the technologies are often applicable to food packaging concepts as well (Brody *et al.* 2001).

Many food products like fresh poultry (protein-rich) and cereal (fat-rich) develop unpleasant odours. Commonly, off-odours produced during protein breakdown include sulphurous compounds like hydrogen sulphide and off-odours produced during lipid oxidation of fats and oils includes aldehydes and ketones. Aldehydes and ketones are also produced during anaerobic glycolysis (Brody *et al.* 2001; Vermeiren *et al.* 2003). Since some odours can be sensed at very low levels, odours that are confined in gas-barrier packages cause an unpleasant smell when opening the package even if the food product is still safe to eat (Rooney 1997).

Another reason to use odour scavengers is that odours may be developed in the packaging material especially during plastic processing like extrusion and molding. Antioxidants are often included as processing additive to reduce the amount of produced off-odours. For example DuPont have incorporated molecular sieves into polyethylene to remove oxidation odours from processing the plastic resin (Brody *et al.* 2001; Rooney 1997; Vermeiren *et al.* 2003).

Work has also been done on incorporating antioxidants like Vitamin E into the resin prior to extrusion to prevent lipid oxidation in dry foods like snack, cereal and bakery products. Vitamin E has therefore been proposed as an alternative antioxidant to butylated hydroxytoluene (BHT) in packaging materials for snacks and hard bakery goods (Brody *et al.* 2001; Brody 2003; Wessling *et al.* 1998). Further it has been shown that polyethylene imine could react with and effectively remove aldehydes and ketons generated during peroxide splitting of unsaturated bonds in lipids (Brody 2003; del Nobile *et al.* 2002). However, these

concepts have not yet been successful commercially. In addition, research is currently about removal of lipid oxidation odours through zeolites, cyclodextrins and activated carbon (Brody 2003). The end-products in lipid oxidation are as mentioned before aldehydes. One of the most promising concepts to increase the shelf life of fatty food products sensitive to oxidation is to use both vitamin E and aldehyde scavenger. Vitamin E, which is an antioxidant, reduces the oxidation rate while the scavenger remove produced odorous compounds (Brody *et al.* 2001; Brody 2003; del Nobile *et al.* 2002). Further concept for reducing the amount of odours is molecular sieves. Molecular sieves of crystalline zeolites with molecular sized organophilic pores that attract and trap odours have been explored by UOP Corporation (Brody *et al.* 2001). The small pores contain cations that adsorb small molecules like odours, while larger molecules are excluded due to steric hindrance (Brody *et al.* 2001; Brody 2002; Brody 2003). Also DuPont has used this technology in their silica-based OTC (odour and taste control) products that reduce flavours developed during plastic processing (Brody *et al.* 2001). (DuPont's scavengers, which were mentioned in the previous section, are incorporated in the plastic material with the purpose to absorb off-odours from deteriorative reactions in the packed food.)

Further example of odour removers includes activated carbon which is both effective and inexpensive and occurs in a number of patents (Parks 1996). Patents in this field also include odour removing compounds like sorbitan monooleat, sodium carbonate, zeolite, potassium bisulfate, citric acid, activated clay, alumina, silica gel, polyalkyl acrylate as well as catechin in tea leaves and chitosan combined with different substrates. Also lignin in paper has shown odour-removing capacity. The paper board may be treated with lignin that adsorbs odours from the paper and additives and therefore prevents them from being absorbed in the packed food (Brody *et al.* 2001).

It has been showed that amines, which are developed during protein breakdown in fish, can be removed by reaction with acidic compounds like citric acid or other food acids incorporated in the plastic layer of the packaging. Also films containing ferrous salt and organic acids have been used for amine removal. The Anico Company Ltd. of Japan markets ANICO BAG, which contains ascorbic acid and ferrous salt dispersed in plastic bags, as preservation of food freshness. Several other freshness indicators have also been marketed in Japan during the latest years, but the effectiveness need to be better demonstrated (Brody *et al.* 2001; Rooney 1997).

#### **2.4.7. Antimicrobial agents**

Antimicrobials in food have been used for a long time, but antimicrobial interactive packaging is a relatively new approach to control microbial surface contamination of foods. There are both migrating and non-migrating antimicrobial systems. Since both require intensive contact between the food product and the packaging material, the primary applications have been vacuum or skin-packed products (Appendini and Hotchkiss 2002; Devlieghere 2000; Vermeiren *et al.* 2002).

Emission of ethanol in the package environment has been shown to extend the shelf life of bakery products. Ethanol lowers the water activity on the food surface and thereby suppresses the growth of some bacteria, yeasts and moulds. Ethicap® is a commercial sachet containing ethanol, silicon dioxide plus a small amount of vanilla or citrus flavour to mask the ethanol. Ethanol vapour is released from the sachet to the headspace of the food package, This technique has been shown to extend shelf life of pre-baked buns from 4 to 17 days. However, a disadvantage of using ethanol emitters is that ethanol is adsorbed by the food product from

the package headspace and the migration limit of 60mg/kg food in the European legislation is easily exceeded (Franke *et al.* 2002; Rooney 1997). Ethanol emitters are widely used in Japan to shelf life extension of bread but also of semi-moist and dry fish products. Ethanol has also been shown to have an anti-staling effect on bread (Day 1999).

Several other antimicrobial agents have been studied including silver-based compounds like Ag-zeolites, organic acids, bacteriocins like nisin and pediocin, hexamethylenetetramine, enzymes like lysozyme, fungicides, and organic compounds like triclosan. However, only few systems have been effective. In addition, strict legislation limit the application of antimicrobial systems (Appendini and Hotchkiss 2002; Brody *et al.* 2001; Franke *et al.* 2002; Vermeiren *et al.* 2002).

#### **2.4.8. Aroma release**

There are several reasons why it is desirable to release aroma compounds into or outside the packaging. First, addition of pleasant aroma compounds may mask unpleasant and bothering odours but it may also be a way to avoid flavour scalping by changing the equilibrium conditions. Further reasons include improvement of the consumer appeal of the food product by amending the aroma precipitation when opening the packaging or attracting the consumers by aroma emitting packaging materials. However, currently most aroma-emitting products are applied in plastic products for non-food applications (Brody *et al.* 2001; Brody 2002).

There are products in this field that are marketed as flavour/polymer alloys, free-flowing pellets, and thermal protection of aroma compounds during plastic processing as well as controlled release of aroma. Polyvel Inc. work with incorporating fragrance or aroma compounds into plastic materials in order to mask unpleasant odours produced during plastic processing, to give a pleasant smell to the final product or to use it in air fresheners. These products are claimed to be compatible with for example PE, PP and EVA. There are however concerns regarding if the thermal stability results in degradation of the flavours especially for sweet flavours as chocolate and also regarding dispersion in the carrier resin and uniform distribution in the end use. A large part of the added fragrance oils are lost during the processing and the final films usually contains about 0,2% aroma compounds (Brody *et al.* 2001).

Another company, Ampacet Corporation, manufactures fragrance concentrates (pine, lemon and baby powder smells) in polyethylene carriers, which are utilized for non-food applications as bathroom and kitchen trash liners. They also produce garbage bags with incorporated fragrances that can withstand high processing temperatures. Further, Dragoco has developed laminations to be used outside the packages releasing aromas upon opening of the package. Aroma compounds are captured by a host material, for example cyclodextrin (modified starch), and placed between plastic laminates. By using a tear strip on the closure which separates the laminates, aroma compounds can be released. With this technology a pleasant smell can be released in packaged fish or as a sweetener in awfully tasting drug. Another advantage is that it can be used for adding volatiles which usually are difficult to mix with plastic (Brody *et al.* 2001).

Further actors in this area are the company Plastiflac, which produce aroma-emitting injection molded plastic products. They add the scent into the plastic melt before injection molding. Vista International Packaging has developed coatings for sausages that contain spices and flavours. Work has also been done on incorporation of aroma compounds into films of silica gel, ethylene vinyl alcohol, polyvinyl chloride etc. However, these films often have poor

mechanical flexibility, short fragrance life and cause problems in the plant production environments. At Dow Corning/Felton Polytrap a polymer-entrapment system with a hydrophobic thermoset polymeric lattice network has been used to hold fragrance and to get controlled release. Application of this product include antimicrobials and animal repellents (Brody *et al.* 2001).

#### ***2.4.9. Modified atmosphere packaging***

There are packaging approaches that not interact with the foodstuff directly, but the adjusted environment within the package increase the shelf life of the packed food product. This concept is called modified atmosphere packaging (MAP). For instance, carbon dioxide is produced and oxygen is consumed during the respiration of fruits and vegetables. By lowering the oxygen content and increasing the carbon dioxide content within the package, the respiration rate and ethylene production of fruits and vegetables are reduced and therefore the shelf life is extended. Research is going on to find the optimal gas composition for each specific fruit, vegetable or other products (Day 1995; Fennema 1996; Floros *et al.* 2000).

## **2.5. Intelligent packaging**

Intelligent packaging is defined by de Kruijf *et al.* as a packaging system that monitor the condition of packed foods to give information concerning the quality of the packaged food during transport and storage (de Kruijf *et al.* 2002). These intelligent packaging concepts will thereby provide better control of food quality as well as higher safety (Yam 2000). Examples of these systems are time-temperature indicators (TTI), leak/gas indicators and freshness indicators.

If the recommended storage temperature is exceeded for some period of time during transport and storage, rapid microbial growth may take place resulting in deterioration of the food product. By using TTI the product quality can be controlled. Presently the most commonly used TTIs show visual colour changes when temperature limits are exceeded. Different physical or chemical principles are used for TTI-indicators including melting point temperature, enzyme reaction, polymerisation, corrosion and liquid crystals (Hurme 2002; Selman 1995).

Gas indicators can be used in modified atmosphere packaging to ensure that the desired environment is kept inside the package and thereby give good food quality. Packaging leaks may also cause contamination of harmful microorganisms resulting in microbial spoilage. Examples of oxygen indicators are redox-dyes and enzyme based systems (Hurme 2002).

Freshness indicators react with volatile metabolites produced during growth of microorganisms and give direct measurements of the microbiological status of the food product. Different freshness indicator systems have been presented for different kinds of food products. For example, hydrogen sulphide has been used for poultry products. There are presently very few commercial freshness indicators. For instance have systems that react with targeted spoilage bacteria or volatile amines of fish with a visual colour change been launched (Hurme 2002).

Another intelligent packaging concept is radio frequency identification (RFID) tags, which consist of mobile databases containing silicon chips and computer technology. These tags carry all details about the product and its history resulting in very good traceability and product control (Bravington 2002). Also temperature switchable membranes have been developed to be used for packaging of fresh fruits and vegetables with specific atmosphere requirements. These membranes are coated with side chain crystallisable (SSC) polymers like siloxanes and acrylic polymers in which the side chain has eight or more carbon atoms. The melting point of the polymer is varied by changing the chain length of the side chains. By choosing appropriate length of the copolymers, desired melting temperature of the material can be achieved but also suitable CO<sub>2</sub>/O<sub>2</sub> permeability ratios. At the specific melting temperature, the SSC polymer switches from its solid, crystalline phase to fluid phase. This results in a dramatic increase in permeability (Clarke 2002).

### 3. Food and packaging interactions

Interactions in packaging include exchange of mass and energy between the packed food, the packaging materials and the external environment. These interactions are classified as mass transfer interactions, biological interactions as well as energy exchange (Hernandez and Gavara 1999). (See table 2) In this review, the focus will be on mass transfer interactions.

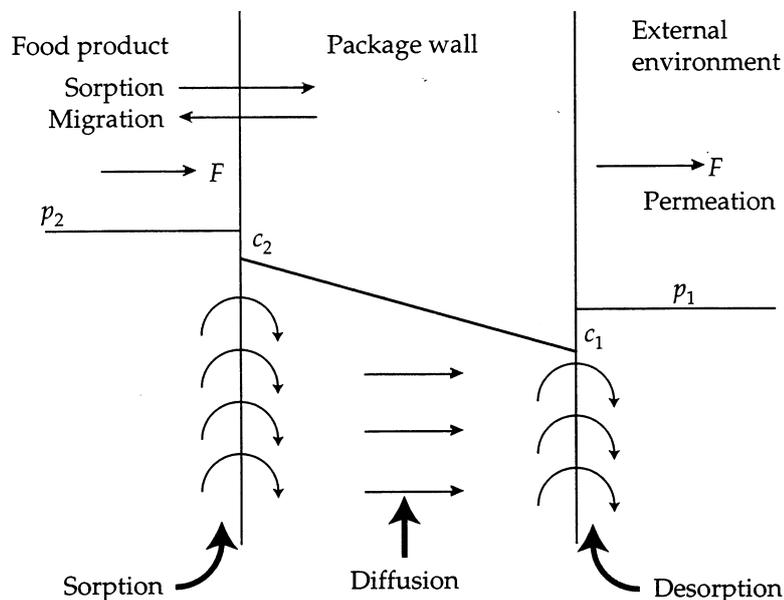
**Table 2.** Food packaging exchanges (Hernandez and Gavara 1999).

Exchange	Principal mechanism	
<b>Mass transfer</b>	Migration into food	Non-volatile and volatile
	Sorption by polymer	Bulk and surface sorption
	Permeation	From inside to outside and v.v.
<b>Biological</b>	Micro-organisms	From the environment
	Macro-organisms	Large organisms from the environment
<b>Energy</b>	Heat transfer	Cooling and heating
	Radiation	UV radiation, visible light, radioactivity

Glass and metal have good barrier properties. (However, glass does not protect against visible light.) Both glass and metal are nearly inert materials resulting in hardly any interactions with the packed food product. On the other hand plastic materials, which are not inert and often have poor barrier properties, commonly interact with the packed food to a large extent (Nielsen and Jaegerstad 1994; van Willige *et al.* 2002).

#### 3.1. Permeation, migration and sorption

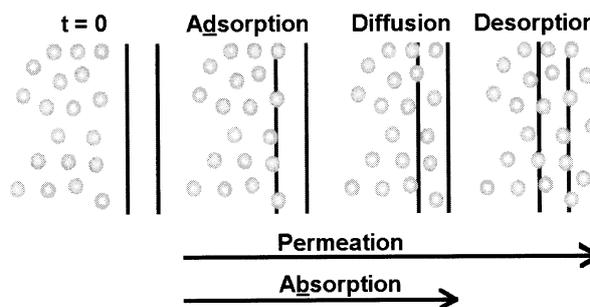
There are three main types of mass transfer in food packaging interactions; **migration**, **sorption** (scalping) and **permeation** (Hernandez and Gavara 1999; Linssen *et al.* 2003; Nielsen and Jaegerstad 1994). (See figure1) Here, migration is defined as package components transferred to the food from the packaging material, while sorption is defined as absorption of food constituents by food contact polymers. Based on thermodynamics laws, the driving force for transfer of components through the packaging material is to achieve equilibrium in the chemical potential of each component (Hernandez and Gavara 1999).



**Figure 1.** Food packaging interactions (Hernandez and Gavara 1999). [ $c_2$ =concentration of compound X in the food product,  $c_1$ =concentration of compound X in the external environment,  $p_2$ =partial pressure of compound X in the food product,  $p_1$ =partial pressure of compound X in the external environment,  $F$ =mass flow.] (Note that these interactions also can also take place in opposite directions.)

Permeation includes three mechanisms; *diffusion* of molecules across the packaging wall as well as *sorption* from the external atmospheres or *desorption* from the internal atmospheres respectively (Crank 1999; Hernandez and Gavara 1999; Mohny *et al.* 1988). Generally, sorption is uptake of food components by the packaging material, which often results in sensory and nutritional changes of the packed food product. Migration is release of compounds from the packaging material to the food product. Examples of possibly migrating compounds are residual monomers, plastic processing additives or components included during material recycling (Crank 1999; Hernandez and Gavara 1999; Mohny *et al.* 1988).

As mentioned above, the permeation process is a multi step process. In the first step molecules collide with the polymer surface and are then adsorbed on the polymer surface and dissolved into the polymer bulk. In the polymer, the permeating molecules move from vacancy to vacancy as the polymer chains move due to their own thermal kinetic energy. This diffusion process results in a net movement of the penetrating molecules from the polymer side in contact with high concentration to the polymer side in contact with low concentration. The last step includes desorption and evaporation of the molecules from the polymer film surface (Delassus 1997). Permeation includes all three steps i.e. adsorption, diffusion and desorption, while absorption (scalping) includes adsorption and diffusion. (See figure 2)



**Figure 2.** Mass transport of molecules through packaging material (van Willige 2002).

The most studied material in terms of scalping is polyethylene in contact with citrus juices (Sadler and Braddock 1990). There are two forms of permeation; transfer of food components through the package to the outside environment as well as transfer of environmental compounds through the package to the food product (Hotchkiss 1995). Most food-packaging interactions are undesirable and reduce the quality of the packed food, but in some cases there are various desirable effects (Hernandez and Gavara 1999; Hotchkiss 1995; Hotchkiss 1997; Sadler and Braddock 1990; van Willige *et al.* 2002).

### 3.2. Laws of diffusion and solubility

Permeation, migration and sorption mechanisms in packaging systems can be described by Fick's laws of diffusion. Fick's laws are applicable for isotropic medium, where the structure and diffusion properties are same in all directions. In Fick's first law of diffusion (1), the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section.  $F$  denotes rate of transfer per unit area,  $C$  is the concentration of the diffusing substance,  $x$  is the space coordinate measured normal to the section and  $D$  is called the diffusion coefficient. In dilute solutions  $D$  is assumed to be constant. If  $D$  varies with time, the diffusion is denoted non-Fickian (Crank 1999; Giacini and Hernandez 1997; Hernandez and Gavara 1999).

$$F = -D \frac{\partial C}{\partial x} \quad (1)$$

If the diffusion coefficient (D) is independent of concentration and if the relationship between the concentration of the penetrating compound and the vapour pressure (p) of the penetrating compound in the surrounding gas phase is linear [i.e. follows Henry's law: C=S·p], then the permeability coefficient (P) is related to the diffusion coefficient (D) and the solubility coefficient (S) by equation (2).

$$P = D \times S \quad (2)$$

When there are interacting compounds, the systems become non-ideal and in that case equations (1) and (2) are no longer applicable. In those cases both concentration and time dependent diffusion processes take place and therefore P, D and S have to be determined independently. Fick's second law of diffusion (3) gives one-dimensional diffusion through an isotropic phase for the unsteady state, where the quantity of permeant, migrant or sorbant changes with time and distance.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

Solutions of the equations above depend on experimental conditions i.e. boundary and initial conditions (Crank 1999; Hernandez and Gavara 1999; Mohny *et al.* 1988). In "The Mathematics of diffusion" written by Clarke (1999), the solutions to the most common systems are compiled (Crank 1999).

The terms used to describe permeability are also expressed as follow (Giacin and Hernandez 1997);

*Mass flow rate:* 
$$F = \frac{q}{At} \quad (4)$$

*Permeance:* 
$$R = \frac{q}{At\Delta p} \quad (5)$$

*Thickness normalized flow rate:* 
$$N = \frac{ql}{At} \quad (6)$$

*Permeability coefficient:* 
$$P = \frac{ql}{At\Delta p} \quad (7)$$

(A=area, Δp=pressure difference of the permeant, q=quantity of permeant passing through the material during time t, l= material thickness, t=elapsed time)

There are several different techniques for measuring the permeability of gases and vapours through polymeric films (Hernandez and Gavara 1999). They can be divided into pressure-variable, volume-variable and isostatic or isobaric methods.

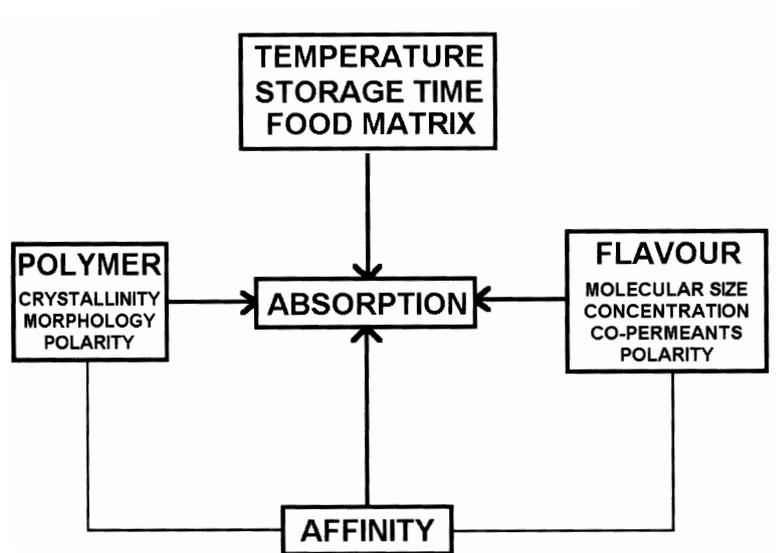
### ***3.3. Parameters affecting the degree of food flavour - packaging interactions***

Adsorption and release of aroma compounds into plastic materials is an equilibrium process i.e. aroma compounds move from high concentration in the food product to the plastic material with lower aroma compound concentration and vice versa (Brody *et al.* 2001). Factors that affect the aroma intensity of packed food products include the vapour pressure of each specific aroma compound, interactions of these volatile aroma compounds with other food components as well as aroma/packaging interactions i.e. the aroma barrier properties of the package (Mohney *et al.* 1988). At high aroma concentrations, the adsorption of the compounds may alter the polymer material by swelling resulting in changed material properties and therefore changed permeability and diffusion coefficients. Volatile compounds tend to interact with the total internal area of the package, while non-volatile compounds will interact only by direct contact between the solid or liquid food phase and the packaging phase. Lower absorption of specific molecules in aroma compound mixtures than in single component mixtures has been noticed. This may be due to interactions between different aroma compounds, competition for free space in the polymer as well as altered solubility of the compounds in the solution (Johansson and Leufvén 1997; Linssen *et al.* 2003; Mohney *et al.* 1988).

Solubility is an important property that affects the extent of food packaging interactions. The **solubility** depends on functional groups in the plastic material and in the aroma compounds, degree of crystallinity of the plastic material as well as molecular weight of solvent molecule. Aroma compounds with similar functional groups i.e. similar polarity as the polymeric material are more easily absorbed in the polymeric material. Since polyolefins are lipophilic, it may not be preferable to use them to pack food products with high amounts of non-polar groups such as fats, oils and aroma compounds. Polyesters, which are more polar, are more suitable for packaging of non-polar products. Crystalline areas in a polymer are much denser than amorphous parts and are therefore almost impermeable to solvent molecules. It has been shown that the sorption of compounds with the same functional groups is increased with increasing number of carbon atoms up to a certain limit (about 10 carbon atoms). For even larger molecules the effect of molecular size is dominating compared to the effect of enhanced solubility by increasing the hydrophobic part i.e. more carbon atoms. Also highly branched molecules are often absorbed more easily than linear molecules. Very large molecules may plasticize the polymer resulting in increased adsorption due to increased surface area (Brody *et al.* 2001; Johansson 1996; Linssen *et al.* 2003). The volatility of aroma compounds, which is essential in flavour precipitation, is dependent on the molecular size (Brody *et al.* 2001; Johansson 1996; Mohney *et al.* 1988).

**Diffusion and permeation** of aroma compounds into or through plastic materials is dependent on glass transition, free volume and porosity of the polymer. Polymers with glass transition temperatures ( $T_g$ ) above ambient temperature e.g. polyethylene terephthalate (PET), polycarbonate (PC) and polyethylene naphthalate (PEN), are stiff and show low diffusion of aroma compounds at low concentrations. On the other hand, polymer with low  $T_g$  e.g. polyethylene (PE) and polypropylene (PP) are softer and have high diffusion coefficients for aroma compounds. A higher degree of crystallinity in a polymer results in lower diffusion. When the free volume in a polymer (the molecular void volume) increases, the mobility of the polymer chains increases resulting in higher diffusion of aroma compounds. In general, polymers with unsymmetrical structures or bulky side groups have high free volumes resulting in high permeability. Absorption of aroma compounds into the free volume of the polymer is also a function of size, flexibility and volatility of the aroma compounds (Brody *et al.* 2001; Linssen *et al.* 2003).

The most important external parameters affecting food-material interactions are temperature and humidity. Increased temperature causes higher permeability of gases and liquids in polymer materials due to increased mobility of flavour molecules and changed polymer material properties by swelling or decreased crystallinity. But increased temperature also results in lower solubility of gases due to the increased volatility. Humidity may decrease barrier properties of some polymeric materials (like EVOH and polyamides) since water acts as a plasticizer. In addition, water vapour may accelerate diffusion of water-soluble components. Polyolefines, PET and amorphous nylon show a slight decrease in oxygen permeability with increasing humidity (Linssen *et al.* 2003).



**Figure 3.** Parameters affecting absorption of food components by the food packaging materials (van Willige 2002).

Factors that affect aroma packaging interactions are summarized into three parts below (Quezada-Gallo *et al.* 2000):

- Properties of volatile compounds such as chemical nature, carbon number, three-dimensional conformation, polarity, solubility, saturated vapour pressure etc.
- Polymer characteristics such as glass transition temperature (T<sub>g</sub>), free volume, monomer properties, density, structure, crystallinity, thickness of the material, surface hydrophobicity etc.
- External conditions like aroma concentration, temperature, pressure, humidity, presence of other permeants such as other food constituents except aroma compounds and also food characteristics as pH, viscosity, texture etc.

### ***3.4. Undesirable effects of food packaging interactions***

Flavour deterioration may be detrimental to the quality of the food product. Substantial amounts of aroma compounds can be absorbed into plastic packaging materials (scalping) or lost by permeation through the packaging material resulting in flavour and aroma loss from the food. Absorption of aroma compounds may also change barrier properties of the plastic. In addition, undesirable odours may be transferred from the plastic or the board to the packed food (Hotchkiss 1995; Hotchkiss 1997; Leufvén *et al.* 1995; Nielsen and Jaegerstad 1994). For example, it has been shown that limonene in orange juice is sorbed into HDPE but not into PS or polylactic acid (PLA) (Haugaard *et al.* 2002). Another study showed that LDPE adsorbed flavour to a greater extent than polycarbonate (PC) and PET. However, this loss of flavour compounds did not influence taste perception (Haugaard *et al.* 2002).

Migration can result in toxicological risks and flavour degradation. Examples of migration phenomena include transfer of plasticizers from polymers and water vapour exchange. This can have both quality and safety consequences (Hotchkiss 1995; Hotchkiss 1997). In addition, metal cans have internal coatings containing the compound 2,2-Bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether (BADGE), which has been found to migrate into some food products (e.g. oil containing foods) to larger extent than is allowed by the migration legislation for this compound (Summerfield *et al.* 1998). Also penetration of oxygen into the package environment is detrimental for the quality of many food products as well as gas loss like carbon dioxide from carbonated drinks or modified atmosphere packages (Hotchkiss 1995; Hotchkiss 1997).

Permeation processes may also change the nutritional quality of the food product. Nutrient loss is often due to high oxygen permeability of the packaging material since oxygen degrades vitamins or is due to light transmission which destroys nutrients like riboflavin in milk (Hotchkiss 1995).

### ***3.5. Desirable effects of food packaging interactions***

Food-packaging interactions can also be used in a positive way. Packaging concepts that reduce the amount of undesirable aromas and flavours, may release aroma compounds, antimicrobials and antioxidants or modify the gas atmosphere have been and are under development. Another benefit of food-packaging interactions is that it is possible to reduce or inhibit oxidation reactions. Further benefits from food-packaging interactions are inhibition of microbial growth (Brody *et al.* 2001; de Kruijf *et al.* 2002; Hotchkiss 1995; Nielsen and Jaegerstad 1994).

All these concepts, which are called active packaging, extend the shelf life or improve the food quality by controlled and desired food-packaging interactions. See chapter 2.4 regarding active packaging)

## 4. Deteriorative reactions in foods

During processing and storage of food products biochemical, chemical, physical and biological changes occur that affect food quality (including texture, flavour, colour, appearance and nutritional value). By using appropriate packaging of the food products, these quality changes may be reduced or removed (Robertson 1993).

### 4.1. Enzymatic reactions

Enzymes, which are complex, globular proteins, act as catalysts in different specific reactions or have regulatory functions in biochemical processes. Enzymatic changes may be desirable for example during fermentation and cheese making but may also be undesirable and result in food spoilage. Examples of undesirable enzymatic reactions in foods include glycolysis in post-mortem, prerigor muscle, oxidation of lipids by lipases and lipoxygenases affecting colour, flavour and texture. Further examples include oxidation of phenolic substances in plants resulting in browning, hydrolysis of phospholipids in fish affecting the texture and sugar-starch conversions in plant tissues. Enzymatic activity is controlled by temperature, water activity, pH, inhibiting chemicals, metal ions and availability of substrates (for example oxygen). Especially temperature, water activity and oxygen level are important factors to control in order to limit enzymatic degradation of the packed food (Robertson 1993).

### 4.2. Chemical reactions

The most common chemical deteriorative reactions in foods include non-enzymatic browning, lipid hydrolysis, lipid oxidation, protein denaturation, protein cross-linking, polysaccharide hydrolysis, protein hydrolysis, polysaccharide synthesis, degradation of pigments and glycolytic changes (Robertson 1993).

One of the major reactions in food deterioration is lipid oxidation resulting in development of undesirable aromas like aldehydes. Polyunsaturated fatty acids and phospholipids are the compounds most susceptible to oxidation due to presence of several double bonds. Oxidation includes four steps. (See figure 4)

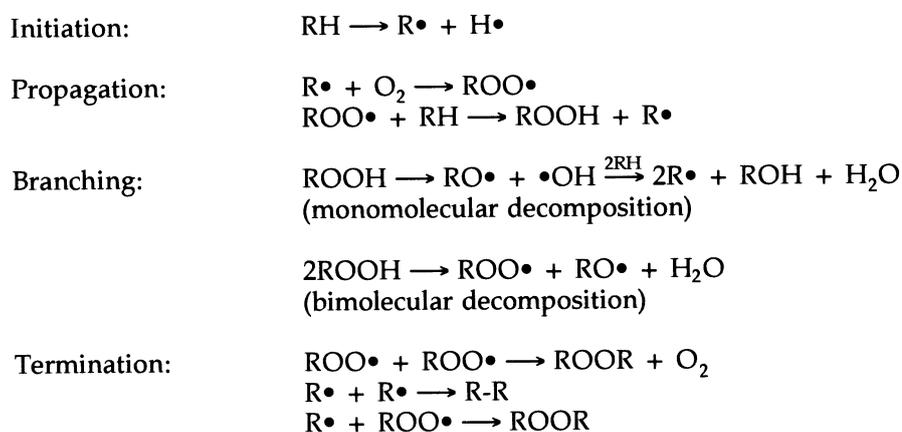


Figure 4. Oxidation reaction mechanism (Robertson 1993).

The first step is initiation when a hydrogen radical is lost due to heat, light or trace metals. Thereafter in the propagation step, the free radical reacts with oxygen forming a peroxy free radical, which in turn reacts with lipids to form a hydroperoxide. During the third step, branching, the number of free radicals increase and hydroperoxides are broken down. Finally, the oxidation process is terminated when free radicals are fused together or when stable radicals are formed. The rate of lipid oxidation can be induced by light, presence of oxygen, high temperature, catalysts like iron, copper and heme pigments as well as water activity (Robertson 1993).

During storage of dried and concentrated foods one of the major deteriorative reactions are non-enzymatic browning also called Maillard reaction. This process can be divided into three parts (Robertson 1993). The first part, which does not include browning but reduce the nutrition value, includes a condensation reaction between an aldehyde and an amine resulting in glycosylamine, which in turn undergoes an Amadori rearrangement. During the second part, the advanced Maillard reactions, several volatile or soluble substances are formed. In the final Maillard reactions, insoluble brown polymers like melanoidin pigments and heterocyclic compounds like pyrazines and pyrroles are produced from reactive compounds formed during the advanced Maillard reactions (Robertson 1993).

The colour of most foods is due to the presence of natural pigments like chlorophylls, heme pigments, anthocyanins, carotenoids, flavonoids and tannins. Chlorophylls are green pigments involved in photosynthesis of plants and can be deteriorated by pheophytinisation i.e. when the magnesium ion within the tetrapyrrole structure is replaced by a hydrogen atom resulting in a colour change from green to brown. This reaction, induced by heat and acids, leads to colour change to some extent in almost all chlorophyll containing foods during processing and storage (Robertson 1993).

The heme pigment myoglobin, which contains an iron atom and a porphyrin ring, gives meat its red colour and functions as storage of oxygen transported by hemoglobin in the blood. However, the colour of fresh meat is changing reversibly by conversion between three pigments; oxymyoglobin, myoglobin and metmyoglobin. These processes can be controlled by appropriate packaging. For example, in the absence of oxygen, the reduced, purple pigment myoglobin is dominating. When oxygen present myoglobin is oxidised to oxymyoglobin, which is a pigment with red colour. When the meat is exposed to air /oxygen for longer times the brown pigment metmyoglobin is most prevalent (Robertson 1993).

Anthocyanins include several red water-soluble plant pigments. Some of these pigments can form complexes with metal compounds like Al, Fe, Cu and Sn resulting colour changes. Therefore metal packaging materials for foods have internal organic coatings to reduce the available metal ions. Carotenoids are yellow or red, lipid-soluble pigments found in plants and animal products. They are broken down by oxidation and the rate of oxidation is dependent on light, heat, and pro- and antioxidants. The yellow pigments, flavonoids, are similar to anthocyanins. Tannins are involved in enzymatic browning (Robertson 1993).

Characteristic flavours in fruits and vegetables are often due to derivatives of fatty acids produced during enzymatic reactions. These reactions can also result in development of unpleasant flavours as during fruit ripening and disrupted tissues. Fats and oils develop off-flavour substances like some aldehydes and ketons through auto-oxidation causing fatty, metallic, papery and candle-like flavours when present in high concentration. (See lipid oxidation above) However, at lower concentrations these compounds give cooked food desirable flavours. Volatile amines like trimethylamine are produced during storage of fish

resulting in ammoniac smelling, fishy aroma. Also formaldehyde is produced in staling fish causing cross linking of proteins and therefore contributing to toughening of the fish muscle (Lindsay 1996; Robertson 1993).

Chemical reactions may also alter the nutritional quality of the food. Even though there are many different kinds of nutrients and they are affected differently by external conditions, the general factors one should control to avoid nutritional loss are light, oxygen concentration, temperature and water activity. For example, ascorbic acid (Vitamin C) is easily deteriorated. To avoid ascorbic acid breakdown, the packaging material should possess barrier properties towards moisture and oxygen and could in addition have a surface which is more easily oxidized than ascorbic acid, like tin. Proteins are mostly deteriorated by oxidation but also by Maillard reactions. Lipids undergo several different kinds of reactions during processing (Robertson 1993).

### ***4.3. Physical changes***

Physical changes of the packed food, which include properties like texture, size, shape, optical, mechanical, rheological etc., depend on handling, processing, packaging and storage conditions. For example powdered food is sensitive to moisture resulting in caking of the product. As mentioned above, chemical reactions in the food product may result in changed physical properties such as staling of fish due to presence of formaldehyde. Physical changes of food quality are often detrimental to the consumer acceptance of the product (Robertson 1993).

### ***4.4. Biological changes***

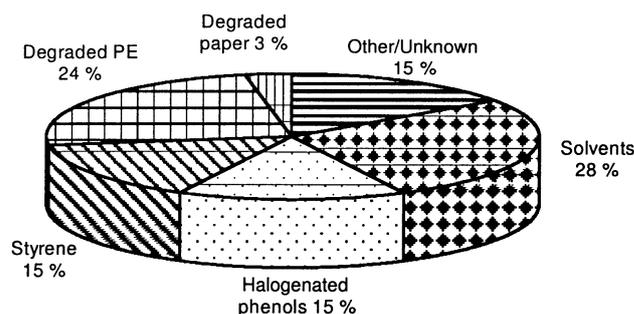
Microorganisms can cause both desirable and undesirable effects during food processing and storage. Microorganisms found in foods are bacteria and fungi (yeasts and moulds). Bacteria generally grow faster than fungi. Based on their stability to resist microorganisms deterioration, foods are classified as non-perishable, semi-perishable and perishable. Examples of a non-perishable food is sugar, which has low water activity and therefore has a very long shelf life if it is stored dry, at room temperature and free from contaminations. Semi-perishable foods include flour, dried fruits, baked goods and frozen foods. However, the majority of foods (meat, fish, milk, fruits and vegetables) are classified as perishable and must be packed properly and stored under controlled temperature conditions. Intrinsic parameters (i.e. the nature of the food) that affect spoilage of the food by microorganisms are pH, water activity, oxidation-reduction potential and nutrient content. Important external parameters include storage temperature, humidity, surrounding gas composition and presence of pinholes in the packaging material. The most common macro-biological spoilage of foods is caused by insects like flies, beetles and moths and also by rodents like rats and mice. Cereals and other foods with a moisture content of at least 12% are often spoiled by mites causing a sour odour in the food. Dairy products, dried fruits, dried and smoked meat, and nuts are often subjected to infestations (Robertson 1993).

As mentioned above, the use of microorganisms during food processing may also be beneficial in different food products by alter and thereby improve the flavour, by preservation or by increasing the nutritional quality. Almost all plant and animal tissues contain enough nutrients required for growth of microorganisms, which may produce both desirable and toxic compounds. By lowering the pH-value and reduce the water activity during the fermentation

process, only a few types of microorganisms will be able to grow (Rose 1982). Fermentation is defined as conversion of agricultural products by enzymatic activities of microorganisms into desirable food products. Fermented foods include bread, dairy products, vegetables and sauces, coffee and cocoa (Djien 1983). Also alcoholic beverages are produced by fermentation. During cheese making, carefully selected bacteria strains are added to the cultures and the choice of strain has a strong influence on the sensory characteristics of each type of cheese (Law 1983). In milk fermentation, the most important process is conversion of the sugar lactose into lactic acid. Further processes in milk fermentation include conversion of citrate into diacetyl, which gives a “buttery”, nut-meat like flavour of dairy products. Acetaldehyde, which is an important flavour compound in yoghurt, is also produced during fermentation especially by some strains (Vedamuthu 1983).

## 5. Odour release from paper and plastic

Odorous compounds from the packaging material may be absorbed by the packed food causing tainting of the food product. Even if these odours are not absorbed by the food, release of unwanted odorous compounds when opening a food packaging generates consumer complaints. Odours in the packaging materials derive from degradation of the components in the packaging materials and their converting processes (printing, coating and lamination) as well as from interactions between the food and the packaging. Also residual monomers and solvents contribute to off-odours (Huber *et al.* 2002; Wiik and Helle 1999).



**Figure 5.** Sources of packaging-related off-flavours in packaging (Huber *et al.* 2002).

In paper, there are numerous extractives that contain unsaturated fatty acids (e.g. linoleic acid). These fatty acids can cause development of rancidity by the production of several different volatile compounds (aldehydes, ketones, alcohols, furans, lower fatty acids, alkenes and alkanes) (Robertson 1993; Wiik and Helle 1999). Most of these compounds are odorous, but it is aldehydes that have the lowest odour thresholds and thus cause the majority of the tainting (Pugh and Guthrie 2000). The most prevalent aldehydes in paper include pentanal, hexanal and heptanal. The “rancidity reactions” continues after the paper has been produced and the odour intensity and the odour characteristics of the paper changes with time (Pugh and Guthrie 2000; Wiik and Helle 1999).

The compounds that cause off-flavours in plastics include carbonyl compounds like aldehydes, ketones, esters and carboxylic acids (Ezquerro *et al.* 2002; Piringer and Rüter 2000; Villberg *et al.* 1997). Most of these have low odour thresholds and are volatile. Additives like antioxidants, plasticizers, solvents and cross linking agents may also cause off-flavours (Villberg *et al.* 1997). In addition, synthetic polymers often contain residual monomers like styrene, vinyl acetate and acrylic esters and residual solvents like ethyl acetate (Piringer and Rüter 2000; Villberg *et al.* 1997). This can cause problems in the packaging of drinking water in bottles of high density polyethylene (HDPE). Off-flavour compounds found in HDPE include 2-propanal, ethyl propanoate, C6-ketone, methylpentenone, toluene, hexanal, 2,4-heptadienal, C7-ketone, ethylcyclohexane, butyl acrylate, C8-ketone, methylhexanal, 2-octenal, nonanal, pentamethylheptane, 1-dodecene and undecadienal. (Ezquerro *et al.* 2002; Piringer and Rüter 2000; Villberg *et al.* 1997) Residual styrene monomers in polystyrene as well as halogenated phenols from wooden fibres cause off-flavours in packaging materials. Further, off-odours in styrene-butadiene coatings may be due to presence of 4-phenyl-cyclohexene, which is produced during a Diels-Alder condensation between styrene and butadiene and which have a very low threshold value. It has also been shown that off-odour problems in coated paper become more intense with increasing moisture content (Huber *et al.* 2002; Piringer and Rüter 2000).

## 6. Legislation

The legislation on food packaging materials i.e. materials intended to come in contact with food differs between Europe, United States of America and Japan (de Kruijf and Rijk 2003; Rossi 2000). The strictest regulations are found in Europe. In 1972, the European Communities started to make efforts to synchronize all existing laws in the field of materials intended to come into contact with food. Rather than harmonize all laws and standards, Directives were drawn up to replace national laws and regulations. [Directive=Community legal acts requiring a national implementation law] The legislation on food contact materials in Europe can be divided into directives applicable to all materials and articles, directives applicable to one category of materials and articles as well as directives related to individual substances (Rossi 2000). The main directives already adopted in the sector of materials intended to come into contact with foodstuffs in the European Community are presented in table 3.

**Table 3.** The main directives already adopted in the sector of materials intended to come into contact with foodstuffs in the European Community (EuropeanParliament 2004; Rossi 2000).

<b>Directives applicable to all materials</b>			
	Framework directive	89/109/EEC	Will be replaced by COD2003/0272
	Symbol	80/590/EEC	
<b>Directives applicable to individual materials and substances</b>			
<b>Plastics</b>	Base directive: monomers	2002/72/EC	Replaces 90/128/EEC
	Directive on the basic rules for migration tests	82/711/EEC	2nd amendment 97/48/EC
	Directive on the list of simulants	85/572/EEC	
	Directive on vinylchloride monomer (VCM)	78/142/EEC	
	Directive on the method for determining VCM in PVC	80/766/EEC	
	Directive on the method for determining VCM in foods	82/432/EEC	
<b>Regenerated cellulose film</b>	Base directive	93/10/EEC	
<b>Ceramics</b>	Base directive	84/500/EEC	
<b>Elastomers</b>	Nitrosamines in teats and soothers	93/11/EEC	

### 6.1. Directives applicable to all food contact materials and articles

In the initial framework, 76/893/EEC, that was adopted in 1978, two general principles were established (Rossi 2000):

- The principle of **inertness** of the material and the **purity** of the foodstuffs.
- The principle of **positive labelling**.

This means that materials and articles must not transfer any components to the packed food that can endanger human health or change the composition and the sensory characteristics of the foodstuff in an unacceptable way. In addition, food contact materials must be appropriated labelled. In 1980, the directive was complemented by regulations for symbols to be attached to food contact materials and articles. In 1989, the framework was replaced by framework 89/109/EEC which included the old directive as well as following regulations: a)The Commission must satisfy rigorous health criteria and consult the Scientific Committee for

Food (SCF) on any regulation with implications as regards health. b) Specific directives and amendments to existing directives will be adopted by the Regulatory Committee procedure. Materials that require legislation comprise plastics including varnish and coatings, regenerated cellulose, elastomers and rubber, paper and board, ceramics, glass, metals and alloys, wood including cork, textile products as well as paraffin and micro-crystalline waxes (Rossi 2000). Directive 89/109/EEC and directive 80/590/EEC will shortly be replaced by a consolidated legislation directive COD(2003)0272. This directive also includes legislation on active and intelligent packaging (EuropeanParliament 2004). (See section 6.3)

## ***6.2. Directive for plastic food contact materials***

In August 2002, the European Commission approved a new directive on plastics intended to come into contact with food, 2002/72/EC, which replaces the old directive 90/128/EEC and its seven amendments (de Kruijf and Rijk 2003; EuropeanCommission. 2003). This directive is based on two principles:

- The **positive list**, which contains all monomers and additives allowed in the production of plastics intended for food contact.
- Limits for total **migration** and for migration of specific components.

The specific migration limits are in general based on the results from extensive toxicological studies where for example acceptable daily intake (ADI) and tolerable daily intake (TDI) are characterised. The overall migration limit is 60mg/kg or 10mg/dm<sup>2</sup> per material or article. There are standards for migration testing in which different food stimulants generally are used, for example water, 3% acetic acid, 15% ethanol and olive oil representing various food products (de Kruijf and Rijk 2003; de Kruijf *et al.* 2002; Rossi 2000).

To add new agents to the EU positive list, results from extensive toxicological studies (including long term exposure, mutagenesis, reproduction, metabolism tests) as well as results from non-toxicological studies (including migration tests) should be submitted to the SCF, which advises the European Commission to accept or decline inclusion of the new components in the directive (Ahvenainen and Hurme 1997; de Kruijf and Rijk 2003; Rossi 2000). This process is both time-consuming and expensive.

This legislation (Directive 2002/72/EC) currently applies only to materials and articles composed of one or more layers exclusively of plastic materials. Consequently, neither paper and paper board coated with plastics or surface coatings with waxes etc. are covered. Paper and board for food contact materials are not yet regulated at EU by a specific directive. Consequently, the Framework Directive 89/109/EEC apply for paper and board in contact with food (EuropeanCommission. 2003). However, within the Council of Europe there is a policy statement concerning paper and board materials and articles intended to come into contact with foodstuffs (Council.of.Europe 2002).

### **6.3. Regulations for active and intelligent packaging**

There are mainly three regulation areas that have impact on active and intelligent packaging in foods; a) all components must be approved for food contact, b) environmental regulations on packaging material usage can be expected to increase in the near future and c) specific labelling of active and intelligent packaging systems are crucial (Rooney 1995).

Until recently no specific legislation for active and intelligent packaging systems existed in Europe. Most of the active and intelligent agents are considered as food contact materials and not as food additives resulting in that these food packaging systems should comply with existing regulations for food contact materials e.g. the active and intelligent agents must be enclosed in the positive list mentioned above and also comply with overall and relevant specific migration limits (de Kruijf *et al.* 2002). As already mentioned, adding agents to the positive list are both time consuming and expensive. In addition, the overall migration limit of 60mg/kg results in that the active agent should be very active at low concentrations, which often is not the case. Further, the contact area in an active packaging differs from conventional packaging, thus established migration tests are not suitable for these new systems (de Kruijf and Rijk 2003).

Amendments to European legislation for food contact materials are necessary and therefore a three-year, European project was started in 1999 with the objective to implement active and intelligent packagings in current relevant regulations for packed food in Europe. The project is called “Evaluating safety, effectiveness, economic-environmental impact and consumer acceptance of active and intelligent packagings” (ACTIPAK) (CT 98-4170). It was coordinated by TNO Nutrition and Food Research in The Netherlands and was accomplished by nine research organisations and three industrial companies. The specific objectives of the project included five main parts (Ahvenainen 2003; de Kruijf and Rijk 2003; de Kruijf *et al.* 2002).

- 1) An extensive **review** of technologies, legislation, market and consumer demands, and trends in active and intelligent packaging in relation to current European food packaging regulations.
- 2) Classification of active and intelligent systems through an **analytical study** of the composition and migration behaviour of selected active and intelligent systems.
- 3) Evaluation of the **safety** of selected systems (such as microbial safety, assessment of the risk for false indications of intelligent systems etc.), the **effectiveness** of the systems’ sensory, microbial and chemical shelf-life-extending capacity as well as the efficiency of the systems as scavengers of different components.
- 4) Examination of **toxicological** properties, **economic** impact and **environmental** effects of selected systems.
- 5) Recommendations for **legislative amendments**.

In the Actipak-project, twenty active systems and six intelligent packaging systems were selected. These are presented in table 4. The criteria in the selection process were to use European systems whenever possible, include as many different types of systems as possible, investigate different mechanisms and include not yet commercial systems.

**Table 4.** Selected active and intelligent packaging systems in ACTIPAK (\*Confidential information) (Ahvenainen 2003; de Kruijf and Rijk 2003; de Kruijf *et al.* 2002).

<b>Active / Intelligent system</b>	<b>Packaging type</b>	<b>Active substance</b>
Oxygen scavengers	Films, closures, sachet	Iron powder, sulphite, photosensitive dye
Moisture absorbers	Sachets, film, pad	Silica gel, molecular sieve, cellulose fiber, sugars
Ethylene scavengers	Film, sachet	Minerals, potassium permanganate
Antimicrobial packaging	Films, sachet	Ethanol, bacteriocin, zinc, acids
Odour and flavour absorber (aldehyde remover)	Film	*
CO <sub>2</sub> -emitting system	Film	*
Flavour/odour releaser	Film	*
Susceptor film	Film	Metallized film
Indicators for time-temperature, oxygen and carbon dioxide	Labels, tablets	Methylene blue and others

The consumer study in the Actipak project showed that consumers accept active agents in food packaging if it results in better food quality or reduction of additives in the food product. Shelf life extension alone was not seen as justification for active packaging. The study also indicated that even if consumers' trust of manufacturers, retailers and government legislation was rather high, assurance that non-harmful chemicals are used in the new packaging systems are needed. Most consumers preferred small labels and sachets kept away from the food product or the active part being incorporated in the packaging material. Further, consumers requested that indicators should be consistent in appearance and colour change to avoid confusion. In addition, the Actipak project also showed economic and environmental advantages by using active and intelligent packaging systems (Ahvenainen 2003; de Kruijf and Rijk 2003; de Kruijf *et al.* 2002).

Based on the results of the Actipak project, a proposal to include active and intelligent systems and make amendments in the directive 89/109/EEC was made in 2003 by the Commission and sent to the Council of Ministers and to the European Parliament. This proposal contained regulations to active and intelligent packaging systems, to labelling, to traceability, and to a detailed description of the procedure for the authorisation of substances. (de Kruijf and Rijk 2003). The proposal has resulted in that the Framework directive 89/109/EEC and directive 80/590/EEC will shortly be replaced by a consolidated legislation directive COD(2003)0272. In this new directive, special regulations of active and intelligent packaging have been implemented. The active components must still be approved to be in contact with food and sufficient labelling of the active and intelligent packaging must be used. Further, it was decided that active and intelligent materials must not change the composition of the packed food or its sensory properties in that way that the consumers will be misled. Consequently, it is not allowed to remove or mask substances (e.g. amines or aldehydes) in order to hide rancidity of the food product. Also active materials that provide colour changes of the food products that can be misleading for the consumers are prohibited (EuropeanParliament 2004).

The Actipak project also showed that migration tests performed according to conventional methods may result in unrealistically high migration values for most active packaging applications. It is proposed that dedicated test methods, which are based on the physical properties of the food as well as on the mode of contact, should be developed (de Kruijf and Rijk 2003).

## 7. Latex coating –an alternative to customary plastic materials

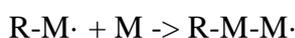
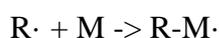
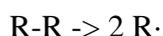
The general definition of latex is colloidal particles (i.e. particle size between 10nm and 1µm) suspended in water (Lee 2000). Suspension is defined as dispersion of solids in liquid. This results in that for example milk is classified as latex. However, mostly latex containing polymer particles are implied. In addition, the name latex is often used for the natural plastic material polyisoprene (Bacquet and Isoard 1997; Strong 2000).

Polymer latexes mainly functions as binders in pigment coating formulations in order to provide improved coating strength, sheet gloss, ink gloss and printability of paper and board (Bergh 1997). However, latex dispersions are also used in barrier dispersion coating, where the latex is applied to the surface of paper or board to form a solid, homogenous film which may possess a barrier against water, water vapour, grease, oil, gas etc (Kimpimäki and Savolainen 1997). The latexes mostly used in paper applications today are mainly polymers or copolymers of styrene, acrylate, methacrylate, butadiene or vinylacetate (Bacquet and Isoard 1997).

For a long time, solvent based coatings were the most prevalent in the paint and coating industry. The trend is nowadays to replace these by aqueous based coatings. The main requirements in coating technologies include good mechanical strength and adhesion of the latex film and good wetting of the substrate (Steward *et al.* 2000).

### 7.1. Latex synthesis

Latex particles are synthesised by radical emulsion polymerisation. The following components are used in this process; monomers (M), water, stabilizing emulsifiers, water-soluble, radical polymer initiator (R) and modifiers (Bacquet and Isoard 1997). The most commonly used radical initiator is persulfate  $S_2O_8^{2-}$  which breaks down to the radical ion  $\cdot SO_4^-$  when heated. The radical reacts with a monomer and a new radical is created, which in turn will react with a new monomer creating a chain reaction as shown below.



The low-water soluble monomers are dispersed in micelle droplets: However, the system is a dynamic equilibrium resulting in exchange of monomers to the aqueous phase. The monomers encounter radicals transforming them to growing macromolecular units which in turn will be encompassed by emulsifying molecules forming micelles. The polymerisation process continues inside of the micelle until another radical penetrates the micelle and reacts with the radical on the growing polymer chain resulting in that the reaction stops i.e. termination. The monomers must contain a double bond to achieve a radical form when reacting with a radical. The main monomers used in latex coating are butadiene, styrene,

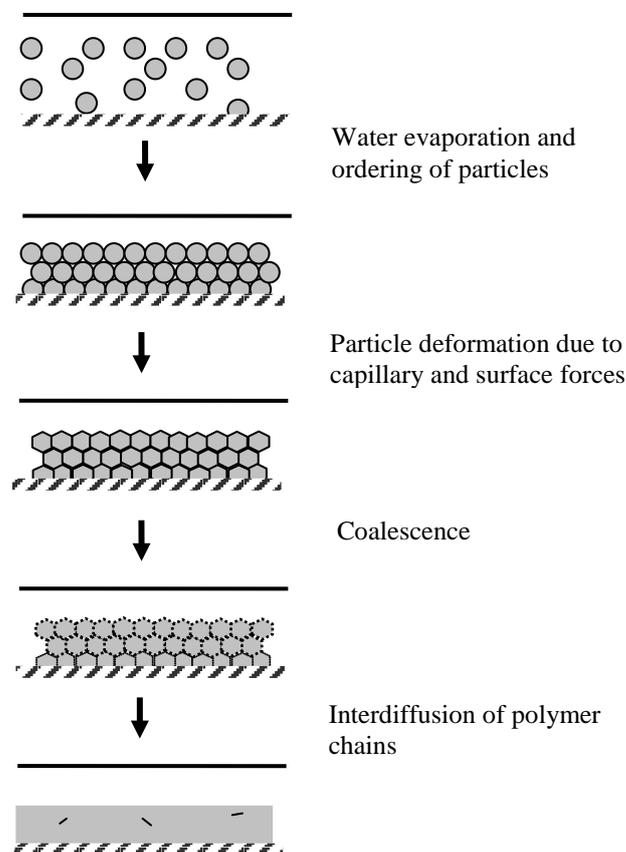
acetate, acrylates and acrylonitrile. In order obtain the desired rigidity, different monomers are combined (Bacquet and Isoard 1997).

## 7.2. Film formation

If latex is applied onto a substrate and is subsequently dried below a certain temperature, a non-transparent, powdery film will be obtained. The opacity indicates that there are still many residual voids, which scatters light, within the film. If however, the film is dried above this certain temperature; a homogenous, transparent film will be obtained. The apparent critical temperature is called the minimum film forming temperature (MFFT). MFFT of a polymer is dependent on the elastic modulus i.e. the resistance to particle deformation and to some extent also to the viscosity of the polymer. The MFFT therefore tend to be close to the glass transition temperature of the polymer ( $T_g$ ) (Dewhurst *et al.* 2001; Steward *et al.* 2000).

To provide better film formation of latex films, volatile organic components are commonly added to latex dispersions as coalescing agents i.e. agents that lower the elastic modulus and provide temporary plasticization to promote polymer chain motion. How easy these components are removed is dependent on molecular size and polarity of the coalescing agents. The more polar component, the more easily it is partition into the hydrophilic net work of evaporating water. Further additives in latex films can be colorants in latex paints or pharmaceuticals in controlled or sustained release matrix-type devices (Steward *et al.* 2000).

The general mechanism for latex film formation includes four main steps: evaporation, elastic deformation, coalescence and interdiffusion (Andersson 2002; Steward *et al.* 2000). (See Figure 6)



**Figure 6.** Film formation of latex polymer coating (Andersson 2002).

During the first step, water evaporates rapidly and latex particles start to get a structured order, but water still fills the interstices among particles. The second step involves the final water evaporation and the particles deform due to capillary and surface forces, but are still individual particles. The surface structure now looks like a honey comb. In the third step, the particles undergo coalescence, which is a process driven by reduction of internal energy. In the final step often referred to as ageing or annealing, the polymer chains diffuse across the particle-particle boundary, the film surface levels and a homogenous film forms (Andersson 2002; Dewhurst *et al.* 2001; Steward *et al.* 2000).

The two last steps can be very fast if the latex particles have a T<sub>g</sub> much lower than the minimum film forming temperature (MFFT). This may result in polymer diffusion starting before all of the bulk water has evaporated and that a small amount of water is trapped inside the bulk. The final evaporation of water occurs therefore by diffusion through the solid phase for low T<sub>g</sub> latex systems. The degree of scattered light is a function of film formation, since the deformation of the latex particles results in reduction of the size and the amount of voids within the film and thus a reduction of the amount of scattered light. A number of theories regarding the driving forces for latex particle deformation have been explored. These theories comprise dry sintering, capillary theory, wet sintering and piston-like compression (Andersson 2002; Dewhurst *et al.* 2001; Steward *et al.* 2000).

### **7.3. Types of latexes**

Styrene and vinyl acetate yields hard polymers while butadiene and butyl acrylate yields soft polymers. The most prevalent latexes in the paper industry are styrene-butadiene latex (70%) and styrene acrylate latex (16%) (Bacquet and Isoard 1997). Products from copolymerisation with acrylic monomers (together with other monomers) will encompass a large variety of physical properties and can be used in a large range of applications. Methacrylate possesses a tough, soft polymer that is almost tack free, while butyl acrylate polymers are soft, plastic and tacky. Except from the monomer types and monomer ratios used, also the degree of cross-linking strongly influences on the properties of the final latex film (Bergh 1997). Typical combinations of monomers are presented below (Bacquet and Isoard 1997).

- Styrene / Butadiene (SB-latex)
- Styrene / Acrylic ester (SA-latex)
- Acrylic ester / Methacrylic ester
- Vinylacetate / Acrylic ester
- Vinylchloride / Vinylidenechloride
- Vinylchloride / Acrylic ester

After purification steps, the solids content and pH is adjusted. Typical properties of latexes are 45-50% w/w solids content, pH 4-8, particle size 0,1-0,2 µm, glass transition temperature -30 to +30°C. The surface tension varies to a great extent between different qualities (Bacquet and Isoard 1997).

Latexes must be chemically and mechanically stable during storage, during shearing of the dispersion formulation with other ingredients and during paper coating (Bacquet and Isoard 1997). Latex particles in dispersions are stabilized by steric and/or electrostatic forces resulting from charged polymer chain end-groups or adsorbed surfactants or polymers like starches. The type of stabilizing components used affects the film adhesion to the substrate (Steward *et al.* 2000). The electrostatic charges on the particles are created by either adding

ionic emulsifiers or use ionic co-monomers ( e.g. vinylic acids like acrylic acid, methacrylic acid, fumaric acid maleic acid etc. but also acrylamide, methacrylamide etc.) during latex synthesis (Bacquet and Isoard 1997; Bergh 1997). By using non-ionic macromolecules with hydrophilic and hydrophobic parts, steric stabilisation, which is independent of pH and ion strength, is achieved (Bergh 1997).

#### **7.4. Latex binders for pigment coating**

Pigment coating improves the printing properties of paper and board by filling the cavities and covering the highest located fibres of the substrate, which achieves a smooth surface with higher gloss. Coating formulations consist of several components including pigments (e.g. minerals like kaolin clay or calcium carbonate), binders (starches, proteins or latecies) and additives like lubricants, pH control agents, foam control agents, colorants, water retention and rheology modifiers etc. Generally, the composition of coating formulations consist of about 100 parts pigments; 10 parts binders and 1 part additives. (Heikkilä *et al.* 2000; Lehtinen 2000).

In pigment coating, the binder shall bind the pigment particles together, bind the pigments to the paper, give the coating formulation a suitable rheology, control the water desorption rate of coating colour, improve stiffness and surface strength, control flatness of the paper sheet, control the penetration of ink in subsequent printing etc. Binders used in the paper industry are divided into two groups; natural (starches and proteins) and synthetic binders (latex dispersions) (Bergh 1997).

The binding power of latecies results from the ability of latecies to form film and wet the surface of pigments (Bacquet and Isoard 1997). To achieve effective bonding both good adhesion and good cohesion are necessary. When increasing the bonding area, the bonding strength also increases. Therefore it is essential that the substrate area is covered to the greatest possible extent and that the binder has good adhesion to the substrate. Good cohesion is achieved when the binder is in a fluid form during the initial stages of the coating process to ensure that as much as possible of the surface of the substrate is covered (Bergh 1997).

#### **7.5. Barrier dispersion coatings**

Barrier dispersion coatings (i.e. latex dispersions) are applied to the surface of paper and board in order to form a solid, uniform film, which possess a barrier against water, water vapour, grease, oil or gases. The most commonly used polymers or copolymers in barrier coatings are styrene, acrylate, methacrylate, butadiene and vinylacetate. Barrier dispersion coatings can be used in both food and non-food applications. When used in food applications, the comprised components must be approved materials for food packaging. (see chapter 6, Legislation). One of the main advantages of barrier dispersion coatings is that they can be fully recycled (by repulping, composting or incineration). Due to the repulpability of dispersion coatings, they are more easily reused than conventional extrusion products (Kimpimäki and Savolainen 1997).

To achieve a good barrier, it is essential that the film is dried perfectly. (Some dispersions contain off-odours due to residual monomers. See Chapter 5, Plastic and paper odour release). The substrate (i.e. paper or board) is important for the odour barrier properties of the packaging. The best odour barrier is achieved by solid boards with well-dried dispersions. A

badly dried dispersion coating will be sensed as much more odorous than a well-dried coating. To achieve a barrier against ultraviolet light, fillers like titanium dioxide, talc and calcium carbonate may be added to the dispersion. Further it is essential to get a pinhole free coating. Pinholes may be created by air bubbles or disordered fibres. Gas barrier properties are essential in many food packaging. Oxygen and carbon dioxide barriers can be made with copolymers of highly polar polymers and non-polar polymers (Kimpimäki and Savolainen 1997).

Until now, the main applications of barrier dispersion coatings have been frozen food cartons, packages for dry food products, wrappings with grease resistance and disposables. However, the development of barrier dispersion coatings is improving and will in the future probably result in packaging materials with higher barrier levels to be used in more demanding food applications (Kimpimäki and Savolainen 1997).

### ***7.6. Surface sizing***

Surface properties of coated paper and board can be significantly improved by using surface sizing. Surface sizing bind fibres and fillers together resulting in that the surface is sealed and hence, reduced porosity, liquid penetration and roughness are achieved. It also improves strength and stiffness of the product, lower dusting tendency and result in better printability. Currently, the most commonly used surface sizing agent for paper and board is starch. Often also minerals are used together with starch in the surface sizing process. Minerals can however induce runnability problems in the paper mill. However, the use of synthetic polymers together with starches in surface sizing is presently growing. These synthetic polymer systems include for instance styrene-maleic-anhydride (SMA), SMA ester and styrene-acrylic-acid copolymer (SAA) solution polymers (Kimpimäki 2001).

## 8. Recycling of packaging materials

The amount of deposited solid waste increases each year. In the United States all packaging material makes up one-third of the total solid waste by weight. Efforts to reduce the solid waste include source reduction, recycling and incineration. The recycling rates of various materials differ (See table 5). Both economic and environmental concerns have resulted in government regulations to promote recycling. The primary concern in using recycled material for food contact packaging is the potential for contaminants in the packed food products (Borchardt 1997; Franz 2002; Pesselman and McCort-Tipton 1999). Food-packaging regulations in Europe require that packaging material must be safe. The migration of harmful recycling-related substances to the food must be excluded and suitable test methods to ensure the safety of recycled materials are needed. An European research project FAIR-CT98-4318 worked with development of suitable test methods for different classes of recycled materials (polyethylene terephthalate, paper and board, and plastics covered with functional barriers i.e. layers of virgin polymer, which is in contact with the food) (Franz 2002; Franz *et al.* 2004).

**Table 5.** Recycling rates of various materials in United States (Borchardt 1997).

<b>Material</b>	<b>Recycling Rate, %</b>
Paper and paperboard	40
Ferrous metals (iron and steel)	37
Aluminium	30
Glass	7
Plastics	1
Rubber and leather	3

As can be seen in table 5, recycling of plastic materials in the US are not yet very common even though this field is likely to expand (Borchardt 1997). The degree of recycling of packaging material is in general a bit higher in Europe than in the US. However, the extent of recycling of packaging material differs between different countries in the Europe. Overall, paper packaging material is the dominating generated recycled material in Europe (Jordan and Heidorn 2003).

There are three stages in recycling of plastics. Primary recycling includes recycling of plant scrap plastics that have not been sold for consumer use. Secondary recycling is physical cleaning and processing of post-consumer plastic products. Tertiary recycling is the chemical treatment of polymers, which usually includes depolymerisation into monomers and then a new polymerisation. During tertiary recycling, fibres and fillers can be removed and the monomers can be purified through distillation prior to the new polymerisation process. Currently, the most important example of tertiary recycling is PET. However, secondary recycling of PET is also common. (Borchardt 1997). Recently, the results of the European research project FAIR-CT98-4318 “Recyclability” showed that post-consumer recycled (PCR) PET materials and articles produced by super-clean technologies (i.e. secondary recycling) can be considered to be safe in direct food applications in the same way as virgin food-grade PET (Franz *et al.* 2004).

However, in many cases packaging consist of paper board coated with plastic materials. Using conventional materials, these plastic laminates must be separated during the recycling process, which is time-consuming, expensive and causes problems during the recycling operation. It is therefore desirable to use a coating that can be readily recycled in the paper mill. Repulpable aqueous-based barrier coatings for paper and board are developed or are under development

that will provide barriers against moisture, water, grease, oils or gases. Some of these are also approved by FDA for food contact (Johnson and Copeland 1999). For example, EvCo Research, Inc. has developed repulpable polyester-based polymers for barrier coating of paper (Salsman 1998). Also Retec Inc. has developed repulpable barrier coatings based on aqueous dispersions of copolymers, which are free of plasticizer. To be easily repulpable, the barrier coating should be recycled directly in the paper mill without any addition of chemicals. Either the coating particles are flushed out of the system or are absorbed into the new paper or board being produced. In addition, the coating should not contaminate the white water systems and must have high enough melting point not to cause stickiness in the pulp process (Johnson and Copeland 1999).

## 9. References

- Ahvenainen, R. (2003). Active and intelligent packaging An introduction. In Novel food packaging techniques. Ed: R. Ahvenainen. Cambridge, Woodhead Publishing Limited: 5-21.
- Ahvenainen, R. and E. Hurme (1997). "Active and smart packaging for meeting consumer demands for quality and safety." Food-Additives-and-Contaminants **14**(6/7): 753-763.
- Andersson, C. (2002). Interactions between polymers in dispersion coating and surface sizing of paper and board. Department of Chemical Engineering. Karlstad University, PhD Thesis.
- Anon (2002). "The new role of packaging." Food-Marketing-&-Technology **16**(1): 45-46.
- Appendini, P. and J. H. Hotchkiss (2002). "Review of antimicrobial food packaging." Innovative-Food-Science-and-Emerging-Technologies **3**(2): 113-126.
- Bacquet, G. and J. C. Isoard (1997). Synthetic latex binders for paper manufacture. In Surface application of paper chemical. Ed: J. Brander and I. Thorn. London, Blackie academic and professional: 48-68.
- Bergh, N.-O. (1997). Binders for paper coating: Starches, proteins and latices. In The Fundamentals of Papermaking Materials. Ed: C. F. Baker. Surrey, Pira International: 139-193.
- Borchardt, J. K. (1997). Recycling. In The Wiley Encyclopedia of Packaging Materials. Ed: A. L. Brody and K. S. Marsh. New York, John Wiley & Sons, Inc.: 799-805.
- Braakman, L. (2002). "The future of PET." Food Engineering and Ingredients **28**(Oct.): 22-25.
- Bravington, C. (2002). Innovative and intelligent RFID technologies for the food industry. In Second International Conference in Active and Intelligent Packaging, 12-13 September, 2002. Ed: L. Brydon. Chipping Campden, CCFRA.
- Brodie, V. and D. L. Visioli (1992). Aldehyde scavenging compositions and methods relating thereto. U.S. Patent. USA, 5,284,892.
- Brody, Strupinsky and Kline (2001). Active packaging for food applications. Lancaster, Technomic Publishing Company.
- Brody, A. L. (2002). "Action in active and intelligent packaging." Food Technology **56**(2): 70-71.
- Brody, A. L. (1992). "Flavor, flavor everywhere -but in packaging?" Packaging **37**(11): 834-835.
- Brody, A. L. (2003). "The sweet smell of food via odor-scavenging packaging." Food-Technology **57**(8): 98-100.

- Clarke, R. (2002). Intelligent packaging for safeguarding product quality. In Second International Conference on Active and Intelligent Packaging, 12-13 September, 2002. Ed: L. Brydon. Chipping Campden, CCFRA.
- Council of Europe (2002). Policy statement concerning paper and board materials and articles intended to come into contact with foodstuffs, Council of Europe, [www.coe.int](http://www.coe.int).
- Crank, J. (1999). The mathematics of diffusion Second edition. Oxford, Oxford university press.
- Crosby, N. T. (1981). Food packaging materials: Aspects of analysis and migration of contaminants. London, Applied Science Publishers.
- Day, B. (1995). Active packaging for fresh produce. In Foods and packaging materials - Chemical interactions. Ed: P. Ackermann, M. Jägerstad and T. Ohlsson. Cambridge, The royal society of chemistry: 189-200.
- Day, B. (1999). "Recent developments in active packaging." Food Review(August): 21-27.
- de Kruijf, N. and R. Rijk (2003). Legislative issues relating to active and intelligent packaging. In Novel food packaging techniques. Ed: R. Ahvenainen. Cambridge, Woodhead publishing limited: 459-496.
- de Kruijf, N., M. van Beest, R. Rijk, T. Sipilainen-Malm, P. Paseiro-Losada and - B.-d. Meulenaer (2002). "Active and intelligent packaging: applications and regulatory aspects." Food-Additives-and-Contaminants **19(suppl.)**: 144-162.
- del Nobile, M. A., G. G. Buonocore, P. Fava and L. Piergiovanni (2002). "Modeling of hexanal sorption kinetic in an aldehydes scavenger film intended for food packaging applications." Food engineering and physical properties **67(7)**: 2687-2691.
- Delassus, P. (1997). Barrier polymers. In The Wiley Encyclopedia of Packaging Technology Second Edition. Ed: K. S. Marsh. New York, John Wiley & Sons: 71-77.
- Dennis, C. (2000). "Future food production and processing trends." Food-Australia **52(10)**: 436-437.
- Dewhurst, J. E., A. S. Drayton-Elder, X. Gao, T. M. Santosusso, C.-F. Tien and T. L. Wickmann (2001). Property development during film formation of two component waterborne polyurethane using dielectric spectroscopy. In Film formation in coatings. Ed: T. Provder and M. W. Urban. Washington, ACS.
- Devlieghere, F. (2000). "The effectiveness of hexamethylenetetramine-incorporated plastic for active packaging of foods." Packaging Technology and Science(13): 117-121.
- Djen, K. S. (1983). Indigenous fermented foods. In Fermented foods. Ed: A. H. Rose. Bath, Academic Press. **7**: 16-38.
- Dunn, T. J. (1997). Multilayer flexible packaging. In The Wiley Encyclopedia of Packaging Technology. Ed: A. L. Brody and K. S. Marsh. New York, John Wiley & Sons: 659-665.

EuropeanCommission. (2003). Food contact materials -Practical guide.  
<http://cpf.jrc.it/webpack/>.

EuropeanParliament (2004). EP-PE\_TC1-COD(2003)0272 Consolidated directive,  
[www.slv.se](http://www.slv.se).

Ezquerro, Ó., B. Pons and T. M.T. (2002). "Development of a headspace solid-phase microextraction-gas-chromatography-mass spectrometry method for the identification of odour-causing volatile compounds in packaging materials." Journal of Chromatography A(963): 381-392.

Fennema, O. R. (1996). Food Chemistry. New York, Marcel Dekker.

Floros, J. D., P. V. Nielsen and J. K. Farkas (2000). "Advances in modified atmosphere and active packaging with applications in the dairy industry." Bulletin-of-the-International-Dairy-Federation **346**(Packaging of milk products): 22-28.

Franke, I., E. Wijma and K. Bouma (2002). "Shelf life extension of pre-baked buns by an active packaging ethanol emitter." Food-Additives-and-Contaminants **19**(3): 314-322.

Franz, R. (2002). "Programme on the recyclability of food-packaging materials with respect to food safety considerations: polyethylene terephthalate (PET), paper and board, and plastics covered by functional barriers." Food Additives and Contaminants **19**(Supplement): 93-110.

Franz, R., A. Mauer and F. Welle (2004). "European survey on post-consumer poly(ethylene terephthalate) (PET) materials to determine contamination levels and maximum consumer exposure from food packages made from recycled PET." Food Additives and Contaminants **21**(3): 265-286.

Giacin, J. R. and R. J. Hernandez (1997). Permeability of aromas and solvents in polymeric packaging materials. In The Wiley Encyclopedia of packaging technology. Ed: A. L. Brody and K. S. Marsh. New York, John Wiley & Sons, Inc.: 724-733.

Haugaard, V. K., C. J. Weber, B. Danielsen and G. Bertelsen (2002). "Quality changes in orange juice packed in materials based on polylactate." European Food Research and Technology **214**(5): 423-428.

Heikkilä, L., A. Tømmerås, T. Engels and E. Knudsen (2000). Coating additives. In Pigment coating and surface sizing of paper. Ed: E. Lehtinen. Helsinki. **11**: 288-302.

Hernandez, R. J. and R. Gavara (1999). Plastic packaging -Methods for studying Mass Transfer Interactions. Leatherhead, Pira International.

Hotchkiss, J. H. (1997). "Food-packaging interactions influencing quality and safety." Food-Additives-and-Contaminants **14**(6/7): 601-607.

Hotchkiss, J. H. (1995). Overview on chemical interactions between food and packaging materials. In Foods and packaging materials -Chemical Interactions. Ed: P. Ackermann, M. Jägerstad and T. Ohlsson. Cambridge, The royal society of chemistry: 3-11.

Huber, M., J. Ruiz and F. Chastellain (2002). "Off-flavour release from packaging materials and its prevention: a food company's approach." Food Additives and Contaminants **19**(Supplement): 221-228.

Hurme, E. (2002). An overview of new intelligent packaging systems for food products. In Second International Conference on Active and Intelligent Packaging, 12-13 September, 2002. Ed: L. Brydon. Chipping Campden, CCFRA.

Hurme, E., T. Sipilainen-Malm, R. Ahvenainen and T. Nielsen (2002). Active and intelligent packaging. In Minimal processing technologies in the food industry. Ed: T. Ohlsson and N. Bengtsson. Cambridge, Woodhead Publishing Limited: 87-123.

Johansson, F. (1996). Food and packaging interactions affecting food quality, PhD Thesis. SIK / Chalmers University of Technology.

Johansson, F. and A. Leufvén (1997). "Concentration and interactive effects on the sorption of aroma liquids and vapours into polypropylene." Journal of Food Science **62**: 355-358.

Johnson, M. and G. Copeland (1999). "Repulpable barrier coating to increase reclaimed OCC." Corrugating International(July): 19-22.

Jordan, K. and C. Heidorn (2003). Wast generated and treated in Europe, European Commission: 32-40.

Kimpimäki, T. (2001). "A new surface sizing concept - a significant decrease in porosity, liquid penetration and surface roughness." Paper Technology **42**(6): 43-48.

Kimpimäki, T. and A. V. Savolainen (1997). Barrier dispersion coating of paper and board. In Surface application of paper chemicals. Ed: J. Brander and I. Thorn. London, Blackie academic and professional: 208-228.

Labuza, T. P. (1996). "An introduction to active packaging for foods." Food-Technology **50**(4): 68-71.

Law, B. A. (1983). Cheeses. In Fermented foods. Ed: A. H. Rose. bath, Academic press. **7**: 148-191.

Lee, D. I. (2000). Latex. In Pigment coating and surface sizing of paper. Ed: E. Lehtinen. Helsinki, PI. **11**: 196-215.

Lee, D. S., D. H. Shin, C. H. Lee, J. C. Kim and H. S. Cheigh (2001). "The use of physical carbon dioxide adsorbents to controll pressure buildup and volume expansion of kimchi packages." Journal of Food Engineering **48**: 183-188.

Lehtinen, E. (2000). Introduction to pigment coating of paper. In Pigment coating and surface sizing of paper. Ed: E. Lehtinen. Helsinki, PI. **11**: 14-28.

Leufvén, A., F. Johansson and C. Hermansson (1995). The influence of food and external parameters on the sorption of aroma compounds in food contact polymers. In Foods and packaging materials -Chemical Interactions. Ed. Cambridge, The royal society of chemistry.

Lindsay, R. C. (1996). Flavors. In Food Chemistry. Ed: O. R. Fennema. New York, Marcel Dekker, Inc.: 723-765.

Linssen, J. P. H., R. W. G. van Willige and M. Dekker (2003). Packaging-flavour interactions. In Novel food packaging techniques. Ed: R. Ahvenainen. Cambridge, Woodhead Publishing Limited: 144-171.

Lopez-Cervantes, J., D. I. Sanchez-Machado, S. Pastorelli, R. Rijk and P. Paseiro-Losada (2003). "Evaluating the migration of ingredients from active packaging and development of dedicated methods: a study of two iron-based oxygen absorbers." Food-Additives-and-Contaminants **20**(3): 291-299.

Matche, R. S. (2001). "New trends in fresh produce packaging." Indian-Food-Industry **20**(6): 58-64.

Mohney, S. M., R. J. Hernandez, J. R. Giacini, B. R. Harte and J. Miltz (1988). "Permeability and solubility of d-limonene vapor in cereal package liners." Journal of Food Science **53**(1): 253-257.

Nielsen, T. and M. Jaegerstad (1994). "Flavour scalping by food packaging." Trends-in-Food-Science-&-Technology **5**(11): 353-356.

Paine, F. A. and H. Y. Paine (1992). A handbook of food packaging. Glasgow, Blackie academic & professional.

Parks, C. J. (1996). Odor-sorbing packages. U.S. Patent. USA, 5,540,916.

Pesselman, R. L. and M. McCort-Tipton (1999). Recycled Plastics: Experimental approaches to regulatory compliance. In Food Packaging: Testing methods and applications. Ed: S. J. Risch. Washington DC, ACS. **753**: 103-113.

Piringer, O. and M. Rüter (2000). Sensory problems caused by food and packaging interactions. In Plastic Packaging Materials for Food: Barrier function, mass transport, quality assurance and legislation. Ed: O.-G. Piringer and A. L. Baner. Weinheim, Wiley-VCH: 407-426.

Piringer, O.-G. and A. L. Baner (2000). Plastic Packaging Materials for Food: Barrier function, mass transport, quality assurance and legislation. Weinheim, Wiley-VCH.

Powers, T. H. and W. J. Calvo (2003). Moisture regulation. In Novel food packaging techniques. Ed: R. Ahvenainen. Cambridge, Woodhead Publishing Limited: 172-185.

Pugh, S. and J. T. Guthrie (2000). "Development of taint and odour in cellulosic carton-board packaging systems." Cellulose(7): 247-262.

Quezada-Gallo, J.-A., D. F. and A. Voilley (2000). Mechanism of aroma transfer through edible and plastic packagings. In Food packaging -Testing methods and applications. Ed: S. J. Risch. Washington DC, ACS. **753**: 125-139.

- Risch, S. J. (2000). New developments in Packaging Materials. In Food packaging: Testing methods and applications, ACS 753. Ed: S. J. Risch. Washington, American Chemical Society.
- Robertson, G. L. (1993). Food packaging: principles and practice. New York, Marcel Dekker.
- Rooney, M. L. (1997). Active packaging. In The Wiley Encyclopedia of Packaging Technology. Ed: A. L. Brody and K. S. Marsh. New York, John Wiley & Sons, Inc.: 2-7.
- Rooney, M. L. (1995). Active packaging in polymer films. In Active food packaging. Ed: M. L. Rooney. Glasgow, Blackie Academic and Professional: 74-110.
- Rooney, M. L. (1995). Overview of active food packaging. In Active food packaging. Ed: M. L. Rooney. Glasgow, Blackie academic and professional: 1-37.
- Rose, A. H. (1982). History and scientific basis of microbial activity in fermented foods. In Fermented Foods. Ed: A. H. Rose. Bath, Academic Press. **7**: 1-13.
- Rossi, L. (2000). European community legislation on materials and articles intended to come into contact with food. In Plastic packaging materials for food. Ed: O. Piringer and A. L. Baner. Weinheim, Wiley-VCH: 393-406.
- Rowan, C. (2001). "The shelf life challenge." Food-Engineering-&-Ingredients **26**(7): 20-23.
- Sadler, G. D. and R. J. Braddock (1990). "Oxygen permeability of low density polyethylene as a function of limonene absorption: An approach to modeling flavour scalping." Journal of Food Science **55**(2): 587-588.
- Salsman, K. (1998). "Waterborne polyester resins in repulpable paper coating." PaperAge(July).
- Selman, J. D. (1995). Time-temperature indicators. In Active food packaging. Ed: M. L. Rooney. Glasgow, Blackie Academic and Professional: 215-237.
- Smith, J. P., J. Hoshino and Y. Abe (1995). Interactive packaging involving sachet technology. In Active food packaging. Ed: M. L. Rooney. Glasgow, Blackie Academic and Professional: 143-173.
- Steward, J. H., J. Hearn and M. C. Wilkinsin (2000). "An overview of polymer latex film formation and properties." Advances in Colloid and Interface Science(86): 195-267.
- Strong, A. B. (2000). Plastics -Materials and Processing. Upper Saddle River, Prentice Hall.
- Summerfield, W., A. Goodson and I. Cooper (1998). "Survey of bisphenol a diglycidyl ether (BADGE) in canned food." Food Additives and Contaminants **15**(7): 818-830.
- Tsai, B. C. and J. A. Wachtel (1990). Barrier properties of ethylene-vinyl alcohol (EVOH) copolymer in retorted plastic food containers. In Barrier polymers and structures, ACS 423. Ed: W. J. Koros. Washington, American chemical society: 192-202.

Wakabayashi, H., Y. Sugihara, A. Hosomi and T. Nakayama (1992). Food preserving agent and method for preserving food with the food preserving agent. Espacenet, Mitsubishi Gas Chemical CO. **EP0504726**.

van Willige, R. W. G. (2002). Effects of flavour absorption on foods and their packaging materials, Wageningen University: 140.

van Willige, R. W. G., J. P. H. Linssen, M. B. J. Meinders, - H. J. van der Stege and A. G. J. Voragen (2002). "Influence of flavour absorption on oxygen permeation through LDPE, PP, PC and PET plastics food packaging." Food-Additives-and-Contaminants **19**(3): 303-313.

Vedamuthu, E. R. (1983). Fermented milks. In Fermented Foods. Ed: A. H. Rose. Bath, Academic press. **7**: 199-223.

Vermeiren, L., F. Devlieghere and J. Debevere (2002). "Effectiveness of some recent antimicrobial packaging concepts." Food-Additives-and-Contaminants **19(suppl.)**: 163-171.

Vermeiren, L., F. Devlieghere, M. van Beest, N. de Kruijf and J. Debevere (1999). "Developments in the active packaging of foods." Trends-in-Food-Science-&-Technology. **10**(3): 77-86.

Vermeiren, L., F. Heirlings, F. Devlieghere and J. Debevere (2003). Oxygen, ethylene and other scavengers. In Novel food packaging techniques. Ed: R. Ahvenainen. Cambridge, Woodhead Publishing Limited: 22-49.

Wessling, C., T. Nielsen, A. Leufvén and M. Jaegerstad (1998). "Mobility of alfa-tocopherol and BHT in LDPE in contact with fatty food simulants." Food Additives and Contaminants **15**(6): 709-715.

Wessling, C., T. Nielsen, A. Leufvén and M. Jaegerstad (1999). "Retention of alfa-tocopherol in low-density polyethylene (LDPE) and polypropylene (PP) in contact with food stuffs and food-simulating liquids." Journal of the Science of Food and Agriculture **79**: 1635-1641.

Wiik, K. and T. Helle (1999). "Mechanisms of paper odor release." Nordic Pulp and Paper Research Journal **14**(4): 268-269.

Villberg, K., A. Veijanen, I. Gustafsson and K. Wickstrom (1997). "Analysis of odour and taste problems in high-density polyethene." Journal of Chromatography A **791**(1-2): 213-219.

Yam, K. L. (2000). "Intelligent packaging for the future smart kitchen." Packaging-Technology-&-Science **13**(2): 83-85.

Zagory, D. (1995). Ethylene-removing packaging. In Active food packaging. Ed: M. L. Rooney. Glasgow, Blackie Academic and Professional: 38-54.