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Active Packaging of Fishery Products: A Review

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Technological advancements are directly reflecting on the consumer's ever increasing demand for healthy, safe and quality food products. Food industry is in search of novel preservation and packaging techniques to cope up with this demand. Active packaging is one such solution to meet this demand effectively. Important active packaging systems include oxygen (O_2) scavengers, carbon dioxide (CO_2) emitter/absorbers, moisture regulators, antimicrobial packaging, antioxidant packaging, ethylene absorbers and flavour releasing and absorbing systems. This article reviews different active packaging systems and their potential applications for fishery products.

Key words : Active packaging, O_2 scavenger, CO_2 emitter, antimicrobial packaging, antioxidant packaging, fish

Food is considered as essential and indispensable to human life. It provides all the elements necessary to develop not only physical but intellectual capabilities also. Quality of life is intimately associated with the diet, as well as the lifestyle of each individual. As there is increasing evidence of linkage between medical conditions such as constipation, cardiovascular diseases, obesity and hypertension to the intake of certain foods, the demand for healthy and convenience food products are increasing world wide. At present, health, nutrition and convenience are the major drivers in the global food industry. Fish and fishery products have attracted considerable attention as a source of important nutritional components like high-quality protein, essential vitamins and minerals and polyunsaturated fatty acids (Ackman, 1989; Ashie et al., 1996). Fish is highly perishable due to the presence of high moisture, protein and highly oxidisable poly unsaturated fatty acids (PUFA), making it vulnerable to various biochemical, physical and microbial forms of deterioration throughout the production chain (catch to retail sale). This leads to the breakdown of protein and lipid fractions and the formation of amines (volatile and biogenic) and hypoxanthine. Enzymatic and chemical reactions are usually responsible for the initial loss of freshness of fish. Microbial activity is responsible for the spoilage making the fish unfit for human consumption, thereby limiting product's shelf life and resulting in heavy economic loss. In spite of the potential health benefits related to fish consumption, eating of fish containing oxidised fatty acids limits the health benefits. The shelf life of fish can be increased by adopting advanced preservation and appropriate packaging.

Over the past few years, there is an increased demand for fresh, mildly preserved convenience foods. In addition, changes in retail and distribution practices associated with globalization, new distribution trends (e.g. internet shopping) and internationalisation of markets, resulted in enhanced distribution distances and storage times. Traditional packaging concepts are limited in their ability to prolong the shelf-life of food products. This encourages the food industry to develop advanced methods for maintaining food quality and extending shelf life. Active packaging is one such advanced and promising technique for food preservation. Active packaging can be defined as a type of packaging that changes the

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condition of the pack and maintains the altered conditions throughout the storage period to extend shelf-life or to improve safety or sensory properties while maintaining the quality of packaged food (Rooney, 1992; Ahvenainen, 2003). Active packaging performs some desiredrole other than providing an inert barrier between the product and external conditions. Active packaging includes gas-flushing, gas-scavenging or emitting systems added to emit (e.g., N_2, CO_2, ethanol) and/or to remove (e.g., O_2, CO_2, odour,) during packaging, storage and distribution. In case of a gas-scavenging or emitting system, reactive compounds are either contained in individual sachets or stickers associated with the packaging material or, directly incorporated into the packaging material. Examples of currently known active packaging systems and their applications relating to fishery products are given in Table 1. The most important active packaging concepts for fishery products include O_2 scavenging, CO_2 emitters, moisture regulators, antimicrobial packaging, antioxidant release, release or absorption of flavours and odours.

O_2 scavenger

Important properties by which consumers judge fish and shell fish products are appearance, texture and flavour (Faustman & Cassens, 1990). Appearance, specifically colour, is an important quality attribute influencing the consumer's decision to purchase. In fresh, red meat fishes, myoglobin can exist in one of three chemical forms. Deoxymyoglobin, which is purple, is rapidly oxygenated to cherry red oxymyoglobin on exposure to air. Over time, oxymyoglobin is oxidised to metmyoglobin which results in brown discoloration associated with a lack of freshness (Faustman & Cassens, 1990). Even very low oxygen concentration is sufficient to initiate oxidation of oxymyoglobin to metmyoglobin (Ledward, 1970). Therefore, in order to minimize metmyoglobin formation in fresh red meats, oxygen must be either reduced to below 0.05% or present at saturation levels (Faustman & Cassens, 1990). High oxygen levels within modified atmosphere package (MAP) also promote oxidation of muscle lipids over time with deleterious effect on fresh food colour (OGrady et al., 1998). Lipid oxidation is a major quality problem in muscle foods resulting in a variety of breakdown products which produce undesirable off-odours and flavours. Therefore, control of oxygen levels in food package is important to limit the rate of deteriorative and spoilage reactions. O_2 absorbing systems provide an alternative to vacuum and gas flushing technologies as a means of improving product quality and shelf life (Ozdemir & Floros, 2004). Although O_2-sensitive foods can be packaged appropriately using modified atmosphere packaging (MAP) or vacuum packaging, these technologies do not always remove O_2 completely. Moreover, the O_2 that permeates through the packaging film cannot be removed by these techniques. Use of an O_2-scavenger, will absorb the residual O_2 in the package and hence quality changes such as discolouration, lipid oxidation and aerobic microbial growth associated with O_2-sensitive foods are minimized (Vermeiren et al., 1999). O_2 scavenging concepts are mainly based on, iron powder oxidation, ascorbic acid oxidation, photosensitive dye oxidation, enzymatic oxidation (e.g. glucose oxidase and alcohol oxidase), unsaturated fatty acids (e.g. oleic or linolenic acid), rice extract or immobilized yeast on a solid substrate (Floros et al., 1997) etc. Scavengers can be characterized by two main properties: absorption capacity and absorption rate. The majority of commercially available oxygen scavengers are based on the principle of iron oxidation (Smith et al., 1990):

$$2Fe \longrightarrow Fe^{2+} + 4e^-$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

$$2Fe^{2+} + 4OH^- \longrightarrow 2Fe\ (OH)_2$$

$$2Fe\ (OH)_2 + H_2O + O \longrightarrow 2Fe(OH)_3$$

The O_2 scavenging sachets are designed to reduce O_2-levels to less than 0.01%. The

Table 1. Some currently known active packaging systems and their applications in food systems

Active packaging system	Substances used	Applications
O_2 scanengers	Chemical systems (powdered iron oxide, catechol, ferrous carbonate, iron-sulfur, sulfite salt-copper sulfate, photosensitive dye oxidation, ascorbic acid oxidation, catalytic conversion of oxygen by platinum catalyst) Enzymatic systems (glucose oxidase-glucose, alcohol oxidase-ethanol vapour)	Fresh and dry fish, sausages, smoked and cured fish
CO_2 emitter	Ascorbic acid, ferrous carbonate, metal halide	Fresh fish and shellfish
Moisture regulator	Silica gel, propylene glycol, polyvinyl alcohol, diatomaceous earth	Fresh and dry fishery products
Ethanol emitter	Encapsulated ethanol	Fresh and Semi dry Fish products
Antimicrobial packaging	Sorbates, benzoates, propionates, ethanol, ozone, peroxide, sulfur dioxide, antibiotics, silver-zeolite, quaternary ammonium salts	Fresh fish and value added products
Antioxidant release	BHA, BHT, TBHQ, ascorbic acid, tocopherol	Fresh fish, dry fish, smoked fish, fish oil,
Flavour absorbing	Baking soda, active charcoal	Fresh and dry fish and shell fish
Flavour releasing	Many food flavours	Fresh and heat processed fish products
Colour containing	Various food colours	Surimi, smoked fish, red meat fish, shrimps
Anti-fogging and anti-sticking	Biaxially oriented vinylon, compression rolled oriented HDPE	Fresh chilled / refrigerated fishery products
Light absorbing / regulating	UV blocking agents, hydroxybenzophenone	Dry fish and fish oil
Microwave susceptors	Metalized thermoplastics	Ready to eat fish meals
Insect repellant	Low toxicity fumigants (pyrethrins, permethrin)	Dry fish, smoked fish and fried fish

rule of thumb is that 1g of iron will react with 300 cc of O_2 (Labuza, 1987). When the initial O_2 concentration at the moment of packing (A) and the O_2 permeability of the packaging material (B) is known, an absorber can be developed with the desired scavenging capacity.

Volume of O_2 at the time of packing (A) can be determined as follows:

$$(A) = (V\text{-}P)\ [O_2]\ /\ 100$$

where,

V = volume of finished pack determined by submersion in water (ml)

P = weight of the finished pack (g)

$[O_2]$ = initial O_2 concentration in the pack (21% if air packed)

Volume of O_2 permeating through the package during storage (B) is determined using the following formula

(B) = S x P x D

where,

S = surface area of the pack (m^2)

P = permeability of the film (ml m^{-2} 24 h^{-1} atm $^{-1}$)

D = expected product shelf life (days)

The volume of O_2 to be scavenged during the storage period is determined by adding A and B. Normally, an absorber with a higher capacity is chosen than calculated capacity to guarantee the total removal of O_2 during the entire storage life of the product. Structurally, the oxygen scavenging component of a package can take the form of a sachet, label, film (incorporation of scavenging agent into the packaging film), card, closure liner or concentrate (Suppakul et al., 2003). O_2 scavenging sachets are not appropriate for liquid foods, as the direct contact of the liquid with the sachet spoil the contents. In addition, sachets may be consumed with food or may be ingested by children accidentally. O_2 scavenging sachets should be labeled “Do not eat” for safety reasons and for regulatory purposes made mandatory by many regulatory agencies including Food and Drug Administration (FDA). Further, the food packs containing O_2 scavenger based on iron powder possess the problem of not passing through the metal detectors. The incorporation of scavengers in packaging film is a better way of resolving sachet related problems. Scavengers may be imbedded into a solid, dispersed in the plastic, or introduced into various layers of the package, including adhesive, lacquer, or enamel layers (Rooney, 1995a).

In enzymatic oxygen scavenging system, an enzyme reacts with a substrate to scavenge oxygen. One example of this system is the use of Glucose oxidase, which is an oxidoreductase that transfers two hydrogens from the –CHOH group of glucose to O_2 with the formation of glucono-delta-lactone and hydrogen peroxide (H_2O_2). The lactone then reacts with water to form gluconic acid (Labuza & Breene, 1989) as below:

$$2G + 2O_2 + 2H_2O \longrightarrow 2GO + 2H_2O_2$$

where G is the substrate.

Since H_2O_2 is an objectionable end product, catalase is introduced to break down the peroxide (Brody & Budny, 1995):

$$2H_2O_2 + \text{catalase} \longrightarrow 2H_2O + O_2$$

Enzyme systems are very sensitive to changes in pH, a_w, salt content, temperature and various other factors. Additionally, they require water for their action and, therefore, cannot be effectively used for dry products (Gra, 1994). These systems are more expensive than iron-based systems, due to the cost of enzymes used for the scavenging purpose. Besides glucose oxidase, other enzymes have showed potential for O_2-scavenging, including ethanol oxidase which oxidises ethanol to acetaldehyde (Labuza & Breene, 1989). Water is not required for the activation of ethanol oxidase and hence can be used for many food systems. However, it requires large quantity of ethanol which may impart off-flavour to the product apart from producing aldehyde as an end product. The enzymes can be part of the packaging structure itself or put in an independent sachet. Polypropylene (PP) and polyethylene (PE) are found to be good substrates for immobilising enzymes (Labuza & Breene, 1989). But the stability of the enzyme in the film over time is questionable.

Another O_2-scavenging technique is based on the principle of photosensitive dye oxidation (Rooney, 1985). This involves sealing of a small coil of an ethyl cellulose film containing a dissolved photosensitive dye and a singlet O_2 acceptor in the headspace of a transparent package. Due to illumination of the film with light of the appropriate wave length, excited dye molecules sensitize O_2 molecules, which have diffused into the polymer, to the singlet state. These singlet O_2 molecules react with acceptor molecules and are consumed (Rooney, 1985):

$$\begin{aligned}
&\text{Photon} + \text{dye} && \longrightarrow \text{Dye}^* \\
&\text{Dye}^* + O_2 && \longrightarrow \text{Dye} + O_2^* \\
&O_2^* + \text{Acceptor} && \longrightarrow \text{Acceptor oxide} \\
&O_2^* && \longrightarrow O_2
\end{aligned}$$

Ascorbic acid is another O_2 scavenging component, which can be incorporated into barrier packaging such as crown caps, plastic or metal closures. The basic reaction is ascorbate oxidizing to dehydroascorbic acid and sulphite to sulphate. The major use is in crown caps to protect beer from oxidation of flavours (Anon, 1998). Some of the commercially available O_2 scavengers are given in Table 2.

Table 2. Commercially available O_2 scavengers

Brand name	Manufacturers
Based on iron powder oxidation	
Ageless®	Mitsubishi Gas Chem Co., Japan
Freshilizer™	Toppan Printing Co., Japan
Vitalon	Toagosei Chemicals Industry Co., Japan
Sanso-cut®	Finetec Co., Japan
Fresh Max™ Fresh Pax™	Multisorb Technologies Inc., USA
Oxysorb®	Pillsbury, USA
ATCO™	Emco Packing Systems, UK and Standa Industries, France
Keplon™	Keplon Co., Japan
Bioka®	Bioka Ltd., Finland
O_2 scavenge films	
Cryovac® OS2000™	Sealed Air Corporation, USA
ZERO2e	CSIRO, Australia
Oxygaurd	Toyo Seikan Kaisha, Japan
O_2 scavenging labels	
Fresh Max®	Multisorb Technologies, USA
ATCO®	Standa Industries, France
Light activated O_2- scavenging film	
Zero 2™	CSIRO, Southcorp Packaging, Australia
OS1000	Cryovac Sealed Air, USA

Most O_2 scavengers in commercial use today are iron-based systems (Smith et al., 1990). Relatively few studies regarding the use of O_2 scavengers in fishery products are reported. Sivertsvik (1997) evaluated the effect of an iron-based O_2 scavenger on different seafood products and reported an extension of shelf life for oxygen-sensitive products. Goncalves et al. (2004) studied the effects of O_2 absorber on the gilthead seabream (Spratus aurata) and reported the extension of shelf-life considerably compared to air packed samples. The effects of iron based O_2 absorber on the quality and safety of fresh water cat fish (Pangasius sutchi) and seer fish (Scomberomorus commerson) during chilled storage were studied (Mohan et al., 2008, 2009a,b). The commercial O_2 absorbers used were effective in reducing the O_2 content in the packs up to 99% within 24h. This decreased O_2 content reduced the oxidative changes, volatile amine formation and total mesophilic bacterial counts significantly compared to air packed samples (Mohan et al., 2008, 2009a, b). The use of O_2 absorber extended the shelf life of catfish to 20 days compared to only 10 days for air packed samples (Mohan et al., 2008). In the case of seer fish, O_2 scavenger packed samples were found acceptable up to 20 days compared to 12 days for control air packed samples (Mohan et al., 2009a). Relatively faster degradation of ATP and presence of its degradation products was reported for seer fish packed in control air packs compared to samples packed with O_2 absorber (Mohan et al., 2009a). Mohan et al. (2009a, b) also reported that the freshness (as K and related values) and safety (biogenic amines formation) were maintained for longer periods in O_2 absorber packed samples compared to control samples. Apart from the shelf life extention, use of O_2 scavenger altered the spoilage microflora of seer fish from gram negative particularly Pseudomonas and H_2S producers to gram positive mainly Brochothrix thermosphacta and Lactobacillus spp (Mohan, 2008). The use of O_2 scavengers is economical compared to vaccum sealing technique. Apart from the advantages, the use of O_2 absorbers also has some disadvantages. An oxygen free atmosphere at a water activity greater than 0.92 can favour the growth of many anaerobic microbial pathogens, including Clostridium botulinum (Labuza & Breene, 1989). The use of oxygen scavengers could be dangerous if the temperature of the product is not kept less than 3.3^0c as higher appropriate temperatures favour the growth of C. botulinum and L. monocytogenes.

CO_2 emitter

In some food products particularly in fish and shellfish products, high CO_2 levels (10-80%) are desirable to suppress microbial growth and to extend the shelf life. CO_2 has a prevailing inhibitory effect on bacterial growth. It is particularly effective against gram-negative, aerobic spoilage bacteria such as Pseudomonas spp. that cause off-colour and odours in fish (Parry, 1993). The effect of CO_2 on bacterial growth is complex and four mechanisms have been identified (Parkin & Brown, 1982; Daniels et al., 1985; Dixon & Kell, 1989; Farber, 1991):

i. Alteration of cell membrane functions including effects on nutrient uptake and absorption

ii. Inhibition of enzymes or decrease in the rate of enzyme reactions

iii. Penetration of bacterial cell membranes, leading to intracellular pH changes

iv. Changes in the physico-chemical properties of proteins

Probably a combination of all these activities account for the bacteriostatic effect. The overall effect of CO_2 is to increase both the lag phase and the generation time of spoilage microorganisms. Over the years, this high CO_2 content in the pack has been achieved by modified atmosphere packaging, in which a package is flushed with a mixture of gases including CO_2 at sufficient levels. However, the concentration of CO_2 within the package will change due to the partial dissolving of CO_2 in to the product and permeability through the packaging film. As, the permeability of CO_2 is 3–5 times higher than that of oxygen in most plastic films, it must be continuously produced to maintain the desired concentration within the package. An active CO_2 generating system can be viewed as a technique complimentary to MAP and oxygen scavenging. The potential of CO_2 in MAP and more recently generation of CO_2 inside the packaging system can be explored in relation to a number of commodities for their successful preservation. Such systems are based on sodium bicarbonate, ascorbate and citric acid. Sodium bicarbonate, when used together with ascorbic acid or citric acid in the presence of water, generates CO_2. This system was used in Europe during the late 1980s to generate CO_2 in MAP of fish. Recently, many commercial sachet and label devices have been developed to emit CO_2. Few examples of commercially available CO_2 emitters are given in Table 3.

Table 3. Commercially available CO_2 emitters and moisture regulators

Brand name	Manufacturers
CO_2 emitters	
Ageless® – G	Mitsubishi Gas Chemical Co., Japan
Fresh Pax® M	Multisorb Technologies Inc., USA
Verifraise Package	SARL Codimer, Paris, France
Freshilizer® C[1] and CW[1]	Toppan Printing Co., Japan
Vitalon® G[1]	Toagosei Chemical Co., Japan
Moisture regulators	
Cryovac® Dryloc®	Sealed Air Corporation, USA
Fresh-R-Paxe	Maxwell Chase Technologies, LLC, USA
Mini Pax® Strip-Pax® Desi-Max®	United Desiccants, USA
Sorb-it® Tri-Sorb® 2-in-1™	Multisorb Technologies, USA
Pichit™	Showa Denko, Japan
Peaksorb®	Peak Fresh Products, Australia

Although use of CO_2 for extending the shelf life of refrigerated fishery products is not new, its use as an active packaging system is yet to gain popularity. Relatively very few studies have been reported on the use of CO_2 emitter for storage of fishery products. Mohan (2008) studied the effect of CO_2 emitters on the quality of seer fish (S. commerson) during chilled conditions. The CO_2 emitter used in the study increased the concentration of CO_2 in the pack up to 80% within 48 h, which inhibited the growth of many microorganisms like Pseudomonads, H_2S producing bacteria including Shewanella putrefaciens. The major spoilage organisms for this high CO_2 atmosphere packs was B. thermosphacta followed by Lactobacillus spp (Mohan, 2008). The high levels of CO_2 also reduced oxidation, formation of volatile and biogenic amines and extended the shelf life of seer fish steaks up to 25 days compared to 12 days for control air packs. However, the colour of meat stored under CO_2 will be slightly greenish which may affect the consumer appeal.

Moisture regulator

Appearance influences significantly on the consumer's attitude towards purchase of any product. The moisture content of fresh fish varies from 75 – 89% depending on the species. When the fish is preserved in chilled conditions in a pack with or without added preservatives, the water leaches out of the whole and cut surfaces of fish product which is known as 'drip'. The metabolism of fat and carbohydrates also produces water. Wet food has a high vapour pressure, and as a result, the humidity in the food package increases. Apart from this, a certain amount of moisture will be released into the packaging during distribution mainly due to the temperature fluctuations (Rooney, 1995b). If this moisture is not removed, this will be absorbed by the product or condensate will be formed, causing microbial spoilage and/or low consumer appeal. Excessively high levels of water causes softening of dry crispy products. Controlling of excess moisture in food packages is important to lower the water activity of the product, to suppress the microbial growth, prevent foggy film formation, and to make the package more attractive to the consumer. An effective way of controlling excess water accumulation in a food package is the use of high barrier film material and the use of moisture scavenger such as silica gel, molecular sieves, natural clay, calcium oxide, calcium chloride and modified starch (Labuza & Breene, 1989; Rooney, 1995b; Day, 1998; Anon, 1998; Suppakul et al., 2003). Among these, silica gel is the most widely used desiccant as it is non-toxic and non-corrosive. Drip-absorbent sheets for liquid water control in high a_w foods such as fish and shell fishes basically consist of a super absorbent polymer in between two plastic film layers which is highly permeable to water vapour. Large sheets are also used for absorption of melted ice in packages of seafood during air transportation. The preferred polymers for absorbing water are polyacrylate salts and graft copolymers of starch (Rooney, 1995b). Another approach to control excess moisture is to capture the moisture in the vapour phase by placing humectants between two layers of a plastic film which is highly permeable to water vapour or by using a moisture absorbent sachet (Anon, 1998). It consists of a humectant propylene glycol film between two sheets of poly-vinyl-alcohol (Labuza & Breene, 1989). The material is marketed for home use for wrapping fish products to reduce the a_w of the food. Controlling moisture of dried fish and shellfishes is also of prime importance as the excess moisture content favours the growth of micro-organisms, causes hydrolytic oxidation and also makes the product soggy. Selection of appropriate packaging with higher barrier property to water vapour can be adopted to overcome this problem. Few commercially available moisture regulators are listed in Table 3.

Antimicrobial packaging

Antimicrobial packaging is a promising form of active packaging especially for fishery products as the microbial contamination of these products occurs primarily at the surface, due to post-process handling. Antimicrobial packaging is aimed to control or even prevent the growth of undesired bacterial species responsible for the packed food product degradation by releasing antimicrobial entities (Bezemer et al., 2000; Cha et al., 2002; Ouattara et al., 2000; Padgett et al., 1998). Antimicrobial food packaging materials extend the lag phase and reduce the growth phase of microorganisms in order to extend shelf life and to maintain product quality and safety (Han, 2000). Antimicrobial active packaging is produced by the addition of volatile and non-volatile antimicrobial agents directly to the polymer, either through antimicrobial adsorption on its surface, antimicrobial immobilization into the polymer by ionic or covalent bonds, or by the use of polymer with antimicrobial activity (Appendini & Hotchkiss, 2002). This type of packaging allows the reduction of the amount of preservative in the foods, satisfying the current consumer demand for processed food with minimum additive levels. In general, the antimicrobial film should be effective against a wide spectrum of microorganisms, effective in low concentrations of the incorporated compounds, cause no alterations in the sensory characteristics of the product, have a compatible cost and comply with the current legislation (Brody, 2001). The antimicrobial compound embedded into the polymer acts in two ways, viz., (i) antimicrobial compound is covalently immobilized into the polymer matrix and acts directly from the film when the food is brought in contact with the active material; and (ii) the preservative is embedded into the matrix in the dry state. When the active material is brought in contact with a moist food, the preservative is released from the material and acts directly on the food.

Antimicrobial films intended for food packaging applications have been studied by several researchers (Chen et al., 1996; Chung et al., 2001; Han & Floros, 1998). A comprehensive list of antimicrobial agents for use in antimicrobial films, containers and utensils are presented in Table 4. The classes of antimicrobial compounds include acid anhydride, alcohol, bacteriocins, chelators, enzymes, organic acids and polysaccharides. Several compounds including organic acids, such as potassium sorbate, sorbic acid, propionate and benzoate have been proposed and/or tested for antimicrobial activity in food packaging (Chen et al., 1996; Han & Floros, 1998) or their respective acid anhydrides (Weng & Hotchkiss, 1993; Weng & Chen, 1997), bacteriocins e.g. nisin and pediocin (Ming et al., 1997), enzymes such as lysozyme (Padgett et al., 1998), metals (Ishitani, 1995) and fungicides such as benomyl (Halek & Garg, 1989) imazalil (Weng & Hotchkiss, 1992), and Ag-zeolite (Ishitani, 1995). The choice of the antimicrobial compound is often limited by the incompatibility of the component with the packaging material or by the heat labile character of the component during extrusion (Weng & Hotchkiss, 1993; Han & Floros, 1997). In contrast to conventional antimicrobial films, some functional groups that have antimicrobial activity have been immobilized on the surface of polymer films (Ozdemir & Sadikoglu, 1998).

Another compound that exhibits antimicrobial effects is ethanol. The use of alcohol to prolong shelf life is a well-known method in food preservation. Ethanol is commonly used as surface disinfectant. The effect of ethanol depends on its concentration. At relatively low concentrations (4-12%), ethanol was proved effective in controlling growth of several moulds and bacteria (Seiler & Russell, 1993; De Kruijf et al., 2002). Spraying ethanol on foods prior to packaging or use of sachets generating ethanol vapour can be adopted. The sachets contain food grade ethanol that is absorbed or encapsulated in a carrier material. A slow or rapid release of ethanol from the carrier material to the package headspace is regulated by the permeability of the sachet material to water vapour. The ethanol in the

Table. 4 Potential antimicrobial agents for food contact applications

Class	Examples
Acid Anhydride	Benzoic anhydride, Sorbic anhydride
Alcohol	Ethanol
Ammonium Compound	Silicon quaternary ammonium salt
Antibiotic	Natamycin
Antioxidant Phenolic	Grape seed extract, pomegranate peel and seed extracts
Bacteriocin	Bavaricin, Lacticin, Nisin, Pediocin
Chelator	Citric acid, EDTA, Lactoferrin, Polyphosphate
Enzyme	Chitinase, Ethanol oxidase, Glucose oxidase, Glucose oxidase, Lysozyme
Fatty Acid	Lauric acid, Palmitoleic acid
Fungicide	Benomyl, Imazalil, Sulfur dioxide
Metal	Copper, Silver
Natural Phenol	Catechin, Hydroquinones
Organic Acid	Acetic acid, Benzoic acid, Citric acid, Lactic acid, Propionic acid, Sorbic acid, Tartaric acid
Organic Acid Salt	Potassium sorbate, Sodium benzoate
Paraben	Ethyl, methyl and propyl paraben
Plant-Volatile Component	Allyl isothiocyanate, Cinnamaldehyde, Eugenol, Terpineol, Thymol
Polysaccharide	Chitosan, carragenan

carrier material is exchanged with the water absorbed by the carrier material. A major disadvantage of ethanol vapour is its absorption by the food product. In some cases, the ethanol concentration in the product might cause regulatory problems. If the product is heated prior to consumption, the accumulated ethanol may evaporate. Another drawback is the cost of the sachets, which limits their use to products with low profit margins (Smith et al., 1995). Ethanol vapour generators are widely used in many countries for high moisture bakery goods, fish products and cheese.

From the food safety point of view, the antimicrobial substances used in the development of active films must have approval to be used in contact with foods due to migration (Weng et al., 1999). Therefore, GRAS (generally recognized as safe) substances such as sorbic acid (Cagri et al., 2001; Limjaroen et al., 2003), benzoic acid, propionic acid (Quattara et al., 2000b; Soares et al., 2002) and its salts (Buonocore et al., 2003; Choi et al., 2005; Ozdemir & Floros, 2001) and nisin (Dawson et al., 2003; Grower et al., 2004; Lee et al., 2004; Melo, 2003) have been reported to be incorporated into polymers for the production of antimicrobial packaging. Sorbic acid and its water soluble salts are widely used as preservatives in fish and meat products. They inhibit or delay the growth of numerous microorganisms, including yeasts, molds, and selective bacteria with effective concentrations in the range of 0.05–0.30 g/100 ml (Sofos & Busta, 1993). Good solubility, stability, and ease of manufacture make potassium sorbate the most widely used form in food systems (Sofos and Busta, 1993). Weng & Hotchkiss (1993) incorporated 1% of benzoic acid anhydrous into low-density polyethylene films, inhibiting completely the growth of Rhyzopus stolonifer, Penicillium spp. and Aspergillus toxicarius in culture medium. Sodium lactate demonstrated antimicrobial efficiency in sausage, when incorporated in cellulose acetate films (Melo et al., 2002). Also, Soares et al. (2002), working with sodium propionate incorporated into cellulose acetate films, found microbial growth inhibition. Melo (2003) reported reduction of 2 log cycles in Staphylococcus sp. count for antimicrobial film incorporated with nisin. Antimicrobial packaging studies have been conducted for both plastic and biodegradable packaging material (Han & Floros, 1997; Weng & Chen, 1997; Lee et al., 1998; Quattara et al., 2000a).

The application of chitosan as antimicrobial agent stems from the cationic charge of chitosan molecule to give rise to aggressive binding onto the microbial cell surface, leading to gradual shrinkage of cell membrane and finally death of the cell. It has been reported that quaternary ammonium salt of chitosan exhibits good antibacterial activities, for example, diethylmethylchitosan chloride showed higher antibacterial activity than chitosan (Harish Prashanth & Tharanathan, 2006). They also noted that the antibacterial activity of chitosan derivatives increased with increasing chain length of the alkyl substituent, and this was attributed to the increased hydrophobicity. Chitosan shows a broad-spectrum antimicrobial activity against both gram-positive and gram-negative bacteria and fungi (Vishu Kumar et al., 2005). However its application as antimicrobial packaging in fishery products has not been reported.

Antioxidant release

Lipid oxidation is one of the main reasons for deterioration of fishery products during processing and storage. Antioxidants are widely used as food additives to improve oxidation stability of fish lipids and to prolong shelf-life, mainly for dried products and O_2-sensitive foods such as fishes as they contain highly unsaturated fatty acids. Antioxidants are substances that can prevent or delay oxidative damage of lipids, proteins and nucleic acids by reactive oxygen species, which include reactive free radicals such as superoxide, hydroxyl, peroxyl, alkoxyl and non- radicals such as hydrogen peroxide, hypochlorous, etc. They scavenge radicals by inhibiting initiation and breaking chain propagation or suppressing formation of free radicals by binding to the metal ions, reducing hydrogen peroxide, and quenching superoxide and singlet oxygen (Shi et al., 2001). Synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), propyl gallate (PG) and tert-butylhydroquinone (TBHQ) are widely used to increase the shelf life, especially of lipids and lipid-containing products by retarding the process of lipid peroxidation. However, BHT and BHA are known to have not only toxic and carcinogenic effects on humans (Ito et al., 1986; Wichi, 1988), but abnormal effects on enzyme systems also (Inatani et al., 1983). Although incorporation of BHT into the packaging film as an antioxidant is widely practiced, of late its use is dwindling due to consumer awareness about nutritional quality and safety of food additives. In response to the growing consumer demand, investigations on antioxidants from natural sources have gained interest (Pokorny, 1991). The research conducted on the antioxidant activities of some plants as natural antioxidants generally focused on the herbs and aromatic plants (Gulcin et al., 2004; Lu & Foo, 2001; Miliauskas et al., 2004; Pizzale et al., 2002; Zheng & Wang, 2001). The antioxidant properties of plant extractshave been attributed to their polyphenol contents (Lu & Foo, 2001; Murthy et al., 2002; Revilla & Ryan, 2000). Many byproducts and wastes generated by agroindustries contain polyphenols with potential application as food antioxidants and preventive agents against some diseases (Torres et al., 2002). It is well known that the grape skins, seeds and stems, waste products generated during wine and grape juice processing, are rich sources of polyphenols (Macheix et al., 1990; Murthy et al., 2002; Saito et al., 1998). Apart from the polyphenols, natural vitamins mainly, C and E, commonly present in fruits can be used as natural antioxidants. Among these, vitamin E has proved to be very stable under processing conditions and has an excellent solubility in polyolefins. However it is confirmed that, vitamin E is a less mobile antioxidant in low density polyethylene (LDPE) than BHT, as vitamin E is a larger molecule (Wessling et al., 1998). Although a wide variety of antioxidants from various sources have been identified, their incorporation in polymer films to exert antioxidative effects is still at the experimental stage.

Release or absorption of flavours and odours

Food packaging materials, particularly some plastics, may interact with food flavours, resulting in loss of flavour known as flavour scalping (Nielsen, 1997). Furthermore, flavours are usually lost or degraded by processing foods at higher temperatures or after packaging. Therefore, there is a need to replace the lost flavour constituents when scalping or degradation occurs. Flavour incorporation in packaging material might be used to minimize flavour scalping. The applications of flavour-enriched packaging materials include the possibility to improve the organoleptic quality of the product by emitting desirable flavours into the food and to pleasant aromas that are released upon opening. Flavour release may also provides a means to mask off odours coming from the food or the packaging. It is of importance that the aforementioned technologies are not misused to mask the microbial off-odours and marketing of products that are below standard or even dangerous for the consumer (Nielsen, 1997).

In contrast to flavour releasing systems, flavour absorbers scavenge undesirable flavours, aromas and odour present in the package headspace. Flavour absorbing systems employ cellulose triacetate, acetylated paper, citric acid, ferrous salt / ascorbate and activated carbon / clays / zeolites to absorb off-odour and off-flavour. Removal of aldehydes from package headspaces was achieved by means of the layer Bynel IXP101 which is a HDPE masterbatch (Rooney, 1995b). Amines can be removed by reacting with acidic compounds e.g citric acid incorporated in polymers (Hoshino & Osanai, 1986).

CO_2 scavenger

In some foods, CO_2 is formed due to deterioration and respiration reactions. The produced CO_2 has to be removed from the package to avoid food deterioration and/or package destruction (Floros et al., 1997), which can be achieved by CO_2 scavenger. The CO_2 scavenging sachet absorb the occluded CO_2 which if not removed would cause the package to burst (Smith et al., 1995). CO_2 absorbers (sachets), consist of either calcium hydroxide and sodium hydroxide, or potassium hydroxide, calcium oxide and silica gel. The CO_2 scavengers can be developed using the active compound $Ca(OH)_2$ which reacts at sufficiently high humidity with the CO_2 to produce $CaCO_3$ (Parry, 1993). Some CO_2-absorbent sachet may also contain CaO and a hydrating agent such as silica gel on which water is adsorbed. The CO_2 scavenging takes place as below (Cullen & Vaylen, 1994):

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Possible applications of CO_2 scavenger include their use in packs of dehydrated poultry products and beef jerkey (Ahvenainen, 2003). Till now the application of CO_2 scavenger for fishery products has not been established.

Ethylene scavenger

Ethylene (C_2H_4) is a growth simulating hormone that triggers ripening, accelerates senescence, induces flowering, accelerates softening, increases chlorophyll degradation, and reduces shelf life of fresh and minimally processed fruits and vegetales (Knee, 1990). To prolong shelf life and to maintain an acceptable visual and organoleptic quality, accumulation of ethylene in the packaging should be avoided. The most well-known, inexpensive and extensively used ethylene absorbing system consists of potassium permanganate embedded in silica (Zagory, 1995). The silica absorbs ethylene, and potassium permanganate oxidizes it to ethylene glycol. Silica is kept in a sachet highly permeable to ethylene, or it can be incorporated into the packaging film. However, potassium permanganate is not integrated into the food contact surfaces of packaging films due to its toxicity (Zagory, 1995). Another type of ethylene scavenging concept is based on the adsorption and subsequent breakdown of ethylene on activated carbon. Other ethylene adsorbing technologies are based on inclusion of finely dispersed minerals such as zeolites, clays and Japanese oya into packaging films (Zagory, 1995). Ethylene scavenger finds its application extensively for fruits and vegetables where as its use for fishery products have not been established yet.

Other active packaging systems

Other active packaging systems that are expected to find increased attention in the future include colour containing films, light absorbing or regulating system, indicators for microwave heating, gas permeable/ breathable films, anti fogging films and insect repellant packages. Food grade colour embedded films can supply colouring compounds to foods that improves the colour and appearance of the product. One possible application of colour releasing systems is in the storage of surimi and imitated products (artificial crab meat). An edible red colour pigment migrates from the surimi wrapper to the product to give the surimi the desirable red colour. Light absorbing or regulating systems protect light sensitive foods from harmful effects of light, especially UV light, by decreasing UV transmittance, thus slowing down the rate of oxidation and enzymatic degradation reactions. Anti-fogging films prevent fog formation inside food packages, such as fresh fish, meat and fruit packages. Anti-fogging films also let customers see packaged foods clearly. Microwave susceptors convert sufficient microwave energy into heat that provides a temperature increase in a very short time compared to conventional heating (Sacharow, 1995). These high temperatures yield drying, crisping and browning effects that are desirable for some food products. Low toxicity fumigants, such as pyrethrins or permethrin can be included to the outer layer of food package against insect attacks during warehousing and transportation (Rooney, 1995b). However being a carcinogen its applications to the food packages is questionable.

Active packaging systems with dual functionality

A more sophisticated way of extending the shelf life of packaged foods with active packaging systems is to use multiple function active systems. For example, the combination of O_2 scavengers with CO_2 and/or antimicrobial releasing systems significantly improves the storage stability of packaged foods. In the packages with O_2 scavenger alone, the removal of O_2 from the package creates a partial vacuum, which may result in the collapse of flexible packaging. Also, when a package is flushed with a mixture of gases including CO_2, the CO_2 dissolves in the product creating a partial vacuum and certain amount of CO_2 permeates through the packaging film. But relatively high CO_2 levels are necessary to inhibit surface microbial growth and to extend the shelf life. In such cases, the self-generating systems, which absorb O_2 and generate sufficient volume of CO_2 will be promising in extending the shelf life of foods particularly fishery products. Such systems are based on either ferrous carbonate or a mixture of ascorbic acid and sodium bicarbonate (Rooney, 1995a).

Future trend

Active packaging systems contribute to the improvement of food safety and extend the shelf-life of the packaged foods. Many of these systems have been proven good for fruits and vegetables and have high potential for preserving fishery products. However, these are evolving technologies in the seafood area and many of these systems are in thedevelopmental stage. Continued innovations in active packaging are expected to lead to further improvements in food quality, safety and stability.

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