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Polypropylene in the Industry of Food Packaging

Somaye Allahvaisi Department of Entomology and Toxicology, Faculty of Agriculture, Islamic Azad University of Tehran, Branch of Sciences & Researches, Iran

1. Introduction

Various pests expose agriculture and food products to attack from storage until consumption by consumers. Insects and fungi are the most serious pests that can contaminate food products in warehouses. Despite modern food and other agricultural products storage and distribution systems, most packaged food products, with the exception of canned and frozen goods, are subject to attack and penetration by insects (Mullen & Highland, 1988). When a packaging containing one of insect life stages enters into storages (infested packaging), it could cause the prevalence of infestation. In addition to reducing food quantity, insects annihilate quality, too. By nourishing into the foods, they prepare the conditions for the attack by pathogen microorganisms, such as fungi and as such, the consumption of these foodstuffs could be followed by dangerous present day diseases e.g. cancer types as contaminated foods to pathogens like fungi are one of the most important problems in the industry of storage foods and they are susceptible to mycotoxins (Jakic-Dimic et al., 2009). There are few categories of mycotoxins regarding their chemical structure, sensitivity of certain organs and origin of fungi that produce them. Aflatoxin is a secondary metabolite produced by Aspergillus flavus (Lopez-Diaz &Flannigan, 1997). Aflatoxin is potential to cause liver damage, cirrhosis, and liver cancer and aflatoxin B1 is the most dangerous toxin for animal and human health (Syarief et al., 2003). So, huge losses have been observed in agriculture produce and different ways are designed for controlling stored-product pests. Storing foodstuffs in bulk or sacks is a usual method for controlling pests without application of chemical methods. These sacks are made of different materials such as sheeted polymers used for packaging agricultural products to prevent the entrance of pests and contaminations (Allahvaisi, 2009). Wastage varies from 5-35% depending on nature of crops. Majority of wastage takes place in each of the steps viz. storage, transportation and at retail market due to improper packaging. Bulk Packaging made of polymers provides a solution for commodities weighing 10-50 kg during handling, storage and transportation, while smaller packaging for food products range from 50 ml to 5kg. Polymeric packaging fulfils the diverse role from protecting products, preventing spoilage, contamination, extending shelf life, ensuring safe storage thereby helping to make them readily available to consumers in our day to day life. This chapter will be a very helpful to

all its readers, entrepreneurs, scientists, existing industries, technical institution, etc in the field of packaging (Anonymous, 2011).

2. Why plastics for packing?

Today, several polymer types are currently used for foodstuff packaging. Plastics have emerged as the most preferred choice of packaging materials for various products- from food, beverages, chemicals, electronic items and so on. They offer unique advantages over conventional materials (Anonymous, 2011):

- Safety: Plastics are safer materials for packaging of food products specially polyolefins which do not react with food. Pilferage and contamination is difficult.
- Shelf Life: Plastics packaging material offer better shelf life
- Cost: Plastics are the most cost effective medium of packaging when compared with any other material, the cost of transportation is reduced considerable on account of lower weight and less damage
- Convenience: Plastics can be converted in any form with various processing techniques, thus can pack any type of substances like liquids, powders, flakes, granules, solids.
- Waste: Packaging in plastics reduces the wastage of various food products, typical example is potatoes or onions packed in leno.
- Aesthetics: A right choice of plastics packaging increased the aesthetic value of products and helps in brand identity
- Handling and Storage: Products packed in plastics are easiest to handle and store as well as transport.
- Plastic products are easy to recycle.

Every day there are new products packed in plastics replacing conventional products and when a thought is given to pack a new product the first choice appears in the mind is Plastic packaging material.

3. Flexible plastic films

In general, flexible plastic films have relatively low cost and good barrier properties against moisture and gases; they are heat sealable to prevent leakage of contents; they add little weight to the product and they fit closely to the shape of the food, thereby wasting little space during storage and distribution; they have wet and dry strength, and they are easy to handle and convenient for the manufacturer, retailer and consumer. The main disadvantages are that (except cellulose) they are produced from non-renewable oil reserves and are not biodegradable. Concern over the environmental effects of non-biodegradable oil-based plastic packaging materials has increased research into the development of 'bioplastics' that are derived from renewable sources, and are biodegradable (Stewart, 1995). However, these materials are not yet available commercially in developing countries. There is a very wide choice of plastic films made from different types of plastic polymer. Each can have ranges of mechanical, optical, thermal and moisture/gas barrier properties. These are produced by variations in film thickness and the amount and type of additives that are used in their production. Some films (e.g. polyester, polyethylene, polypropylene) can be 'oriented' by stretching the

material to align the molecules in either one direction (uniaxial orientation) or two (biaxial orientation) to increase their strength, clarity, flexibility and moisture/gas barrier properties. There are thus a very large number of plastic films and small-scale processors should obtain professional advice when selecting a material to ensure that it is suitable for the intended product and shelf life. Typically, the information required includes: type of plastic polymer(s) required; thickness/strength; moisture and gas permeability; heat seal temperature; printability on one or both sides; and suitability for use on the intended filling machinery (Ramsland, 1989; Robertson, 1993). Some may offer virtually no resistance against insects while others may be extremely resistant (Highland, 1981). Plastics based on Polypropylene (PP), polyethylene (PE), Polyvinylchloride (PVC) and Cellophane is mainly used for packaging applications (Table 1) (Odian, 2004).

| Properties | Polye | thylene | Polypropylene | Polyvinyl chloride | Cellophane |
|--|----------------|-----------------|---------------|-----------------------|------------|
| Max. heat tolerance (°C) | 82 | 2-93 | 132-149 | 66-93 | 90-140 |
| Min. heat tolerance (°C) | -57 | | -18 | -46 to -29 | -77 |
| Sun light resistance | | erate to ood | moderate | good | good |
| Gas transmission | O ₂ | 500 | 160 | 8-160 | 122-480 |
| | N_2 | 180 | 20 | 1-70 | 33-90 |
| $(mm/100 \text{ cm}^2 \text{ in } 24 \text{ h and } 25^{\circ}\text{C})$ | CO_2 | 2700 | 540 | 20-1900 | 2220 |
| H ₂ O Absorption % | < | 0.01 | < 0.05 | 0 | < 0.03 |
| H ₂ O Vapor transmission (g/100 cm ² in 24h & 37.8°C & R.H. 90%) | 1 | -1.5 | 0.25 | 4-10 | 0.2-1 |

Table 1. Some properties of used different polymers for packaging foodstuffs

A summary of the main different types of flexible plastic films is as follows (Anonymous, 2008):

3.1 Cellulose

Plain cellulose is a glossy transparent film that is odourless, tasteless and biodegradable (within approximately 100 days). It is tough and puncture resistant, although it tears easily. It has dead-folding properties that make it suitable for twist-wrapping (e.g. sugar confectionery). However, it is not heat sealable and the dimensions and permeability of the film vary with changes in humidity. It is used for foods that do not require a complete moisture or gas barrier, including fresh bread and some types of sugar confectionery. Cellulose acetate is a clear, glossy transparent, sparkling film that is permeable to water vapour, odours and gases and is mainly used as a window material for paperboard cartons (Chiellini, 2008).

3.2 Polyethylene (or polythene)

Low-density polyethylene (LDPE) is heat sealable, inert, odour free and shrinks when heated. It is a good moisture barrier but is relatively permeable to oxygen and is a poor

odour barrier. It is less expensive than most films and is therefore widely used for bags, for coating papers or boards and as a component in laminates. LDPE is also used for shrink- or stretch-wrapping (see Technical Brief: Filling and Sealing Packaged Foods). Stretch-wrapping uses thinner LDPE ($25 - 38 \mu m$) than shrink-wrapping ($45-75 \mu m$), or alternatively, linear low-density polyethylene is used at thicknesses of $17 - 24 \mu m$. The cling properties of both films are adjusted to increase adhesion between layers of the film and to reduce adhesion between adjacent packages (Fellows & Axtell, 2003). High-density polyethylene (HDPE) is stronger, thicker, less flexible and more brittle than LDPE and a better barrier to gases and moisture. Sacks made from HDPE have high tear and puncture resistance and have good seal strength. They are waterproof and chemically resistant and are increasingly used instead of paper or sisal sacks.

3.3 Polypropylene

Polypropylene is a clear glossy film with a high strength and puncture resistance. It has a moderate barrier to moisture, gases and odours, which is not affected by changes in humidity. It stretches, although less than polyethylene. It is used in similar applications to LDPE. Oriented polypropylene is a clear glossy film with good optical properties and a high tensile strength and puncture resistance (Bowditch, 1997). It has moderate permeability to gases and odours and a higher barrier to water vapour, which is not affected by changes in humidity. It is widely used to pack biscuits, snackfoods and dried foods (Hirsch, 1991).

3.4 Other films

Polyvinylidene chloride is very strong and is therefore used in thin films. It has a high barrier to gas and water vapour and is heat shrinkable and heat sealable. However, it has a brown tint which limits its use in some applications. Polyamides (or Nylons) are clear, strong films over a wide temperature range (from – 60 to 200°C) that have low permeability to gases and are greaseproof. However, the films are expensive to produce, require high temperatures to heat seal, and the permeability changes at different storage moistures. They are used with other polymers to make them heat sealable at lower temperatures and to improve the barrier properties, and are used to pack meats and cheeses (Paine & Paine, 1992).

3.5 Coated films

Films are coated with other polymers or aluminium to improve their barrier properties or to impart heat sealability. For example a nitrocellulose coating on both sides of cellulose film improves the barrier to oxygen, moisture and odours, and enables the film to be heat sealed when broad seals are used. Packs made from cellulose that has a coating of vinyl acetate are tough, stretchable and permeable to air, smoke and moisture. They are used for packaging meats before smoking and cooking. A thin coating of aluminium (termed 'metallisation') produces a very good barrier to oils, gases, moisture, odours and light (Lamberti and Escher, 2007). This metallised film is less expensive and more flexible than plastic/aluminium foil laminates (Lamberti & Escher, 2007).

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3.6 Laminated films

Lamination (bonding together) of two or more films improves the appearance, barrier properties or mechanical strength of a package (Ramsland, 1989).

3.7 Coextruded films

Coextrusion is the simultaneous extrusion of two or more layers of different polymers to make a film. Coextruded films have three main advantages over other types of film: they have very high barrier properties, similar to laminates but produced at a lower cost; they are thinner than laminates and are therefore easier to use on filling equipment; and the layers do not separate. There are three main groups of polymers that are coextruded:

- Low-density and high-density polyethylene, and polypropylene.
- Polystyrene and acrylonitrile-butadiene-styrene.
- Polyvinyl chloride.

Typically, a three-layer coextrusion has an outside layer that has a high gloss and printability, a middle bulk layer which provides stiffness and strength, and an inner layer which is suitable for heat sealing. They are used, for example, for confectionery, snack-foods, cereals and dried foods. Thicker coextrusions (75 - 3000 μ m) are formed into pots, tubs or trays.

4. Polymer films for packaging foodstuffs

Polymeric films have the most application in industry and are used in many packaging applications specially greenhouse and agricultural. In agricultural products that is the important subject in packaging, there are specific products include cereal, spices, edible oils, drinking water, chocolate and confectionery, fruits and vegetables, marine products and many more. So, there are various food items those are effectively and economically packed in various types of plastic packaging materials.

4.1 Physical properties of polymers

Physical properties of polymers include the degree of polymerization, molar mass distribution, crystallinity, as well as the thermal phase transitions:

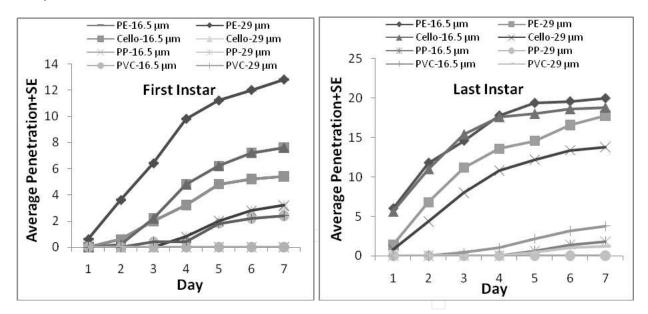
- Tg, glass transition temperature
- Tm, melting point (for thermoplastics).

A plastic film suitable for use in fabricating a trash bag must exhibit strong physical properties in order to resist internal and external stresses on the bag. Such a bag could also be suitable for use as a container for shipping goods. In addition to resisting stresses, it is highly advantageous if the plastic film is easily heat sealable in order to simplify the manufacturing operations for producing the bags. The heat sealed seams must be strong and be capable of resisting stresses tending to break the seams (Liu et al., 2004).

4.1.1 Packaging polymers for preventing penetration of pest insects

Although finished products can be shipped from production facilities uninfested, stored product insects can enter packaged goods during transportation, storage in the

warehouse, or in retail stores. As from storage to consumption by consumers, the agriculture products are exposed to attack by pest insects. Insects are the most serious pests that can contaminate the food by penetration of products in warehouses. The packaging of products is the last line of defense for processors against insect infestation of their finished products. There are two types of insects that attack packaged products: "penetrators", which are insects that can bore holes through packaging materials; and "invaders", which are insects that enter packages through existing holes, such as folds and seams and air vents (Highland, 1984; Newton, 1988). The most insects use their sense of olfaction to find food. The foodstuffs packages are made of different materials such as sheeted polymers which are used for packaging the agricultural products in order to prevention of entrance of pests. Consumer-size food packages vary considerably in their resistance to insects. Sometimes the contamination was created by entrance of one infested package. When neglected, such an infestation will serve as a source of infestation for other commodities in the storage area. So, the packaging polymers should not only be resistance to insects, but also should be permeable to gases used for disinfecting in stores. Thus, the polymer thickness and manner of placing packages in storage should be corrected to prevent serious damage in the products (Cline, 1978). Although, the polymer's kind is more important than thickness. In a study determined that the difference between thicknesses of 16.5 and 29 µm is significant (Fig. 1). This figure shows that the ability of species to penetrate materials may vary between life stages (Allahvaisi, 2010).



(PE=polyethylene, PP=polypropylene, PVC=polyvinylchloride and Cello=cellophane)

Fig. 1. Number of first and last instar larvae of *S. cerealella* that penetrated tested polymeric pouches with two thick in lack of food conditions during 7-d period

As, remaining constant and subsequently decreasing the slope of the curves at insects' penetration last days (after maximum penetration) prove that insects always attempt to penetrate new food packages and their high activity is for availability to more food sources. In bottom table you see the permeability percentage of four current polymers for packaging foodstuffs in two thicknesses to some stored-pest insects starved.

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| | Р | est insecs` | s penetratio | n in polyn | neric pack | agings (A | Average±8 | SE) | |
|-------------------|--------------|---------------|----------------|----------------|----------------|--------------------|---------------|-----------------|---------------|
| Polymer | Polyethylene | | | Cellop | hane | Polyvinyl chloride | | | |
| Thickness (μm) | | 16.5 | 29 | 16.5 | 29 | 16.5 | 29 | 16.5 | 29 |
| | А | 12±0.45 | 4.2±0.36 | 13.8±0.5 | 6.4±0.76 | 3.6 ± 0.4 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 1 | а | b | а | С | С | d | d | d |
| T. castaneum | F | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | L | 11.45±0.0 | 3.8±0.36 | 10.6 ± 0.4 | 3.4 ± 0.4 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 2 | | | | | | | | |
| О. | А | 4±0.54 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| surinamensis | 4 | | | | | | | | |
| C. maculates | А | 9±0.31 | 2.4 ± 0.22 | 6.2±0.36 | 5.4 ± 0.22 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| C. muculules | 3 | | | | | | | | |
| | А | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | F | 15.6±0.5 | 9.2±0.5 | 12.2 ± 0.5 | 3.6±0.22 | 2.4±0.24 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| T. granarium | 1 | а | С | b | d | e | f | f | f |
| | L | 20±0.5 | 19.2 ± 0.4 | 20±0.002 | 18.2 ± 0.4 | 10 ± 0.45 | 2.4 ± 0.7 | 3.6±0.93 | 0.0 ± 0.0 |
| | 1 | а | а | а | а | b | С | С | d |
| | F | 8.8±0.36 | 3.6±0.22 | 5.8±0.36 | 5.8±0.36 | 1.8±0.2 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| P anardraula | 1 | b | d | а | d | С | e | d | f |
| B. amydraula | L | 20±0.002 | 18.02±0.32 | 19.4±0.22 | 18.6 ± 0.4 | 7.6±0.22 | 5.4±0.22 | 10.4 ± 0.22 | 3.4±0.22 |
| | 1 | а | а | а | а | b | d | с | e |

(1: Being Bilateral Effect and Duncan's Test Grouping , 2: Disbilateral Effect of Polymer and Thickness , A: Adult, F: First Instar Larvae , L: Last Instar Larvae , 3: Being Bilateral Effect , 4: T-value)

Table 2. Average permeability percentage of different polymers to major stored-product insects in state of without food

Packaging polymers with repellents for preventing penetration of pest insects

In addition to improving the packaging material and design, insect repellents are used to prevent insects from entering packages by modifying the behavior of insects (Highland, 1984; Mullen, 1994; Watson and Barson, 1996; Mullen and Mowery, 2000). Pyrethrins synergized with piperonyl butoxide were approved for use as a treatment for insectresistant packaging on the outer layer of packages or with adhesive in the USA (Highland, 1991). The repellency of pyrethrins was the primary mode of action against insect penetration and invasion (Laudani & Davis, 1955). Methyl salicylate, an insect repellent, has been registered to be used in food packaging to control stored-product insects in the USA (Radwan & Allin, 1997). DEET, neem, and protein-enriched pea flour are repellent to manystored-product insects when tested by exposure on filter paper or in preference chambers (Khan & Wohlgemuth, 1980; Xie et al., 1995; Fields et al., 2001). Included in the construction of the multiple-wall bags was a barrier layer that prevented the migration of repellents into the foodstuffs. So, a resistant polymer to insect's penetration with a repellent of pests is the most suitable cover for packaging because it can prevent insect penetration and can be as a safe method for IPM programs which could in further reduce the application of the synthetic chemical pesticides and prevent the infestation of the stored-product pests. In some researches polypropylene polymer films are introduced as a suitable polymer with repellent for controlling the pest insects of stored-products. Research performed by Hou and colleagues (2004) showed that the repellents such as DEET reduce the number of insects entering the envelopes (Table 3).

| Number | of insects | | Р | |
|---------|---|---|--|--|
| Treated | Treated Untreated | | ľ | |
| 270.3 | 18973 | 735.82 | < 0.0001 | |
| 1773 | 10178 | 197.88 | < 0.0001 | |
| 470.7 | 117728 | 354.1 | < 0.0001 | |
| 1173 | 10078 | 246.77 | < 0.0001 | |
| 3475 | 507731 | 1481.56 | <0.0001 | |
| | Treated 270.3 1773 470.7 1173 | 270.318973177310178470.7117728117310078 | TreatedUntreated χ^2 270.318973735.82177310178197.88470.7117728354.1117310078246.77 | |

Table 3. Number of insects (\pm SEM) in envelopes treated with DEET at 50 ml/envelope, 1 week after insects were released (n = 4)

4.2 Chemical properties of polymers

The attractive forces between polymer chains play a large part in determining a polymer's properties. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. Also, longer chains are more amorphous (randomly oriented). Polymers can be visualised as tangled spaghetti chains - pulling any one spaghetti strand out is a lot harder the more tangled the chains are. These stronger forces typically result in high tensile strength and melting points. The intermolecular forces in polymers are determined by dipoles in the monomer units. Polymers containing amide groups can form hydrogen bonds between adjacent chains; the positive hydrogen atoms in N-H groups of one chain are strongly attracted to the oxygen atoms in C=O groups on another. These strong hydrogen bonds result in, for example, the high tensile strength and melting point of Kevlar (Anonymous, 2011).

4.2.1 Polymers and permeability to fumigants for controlling pests through packages

In spite of the advances recorded in many aspects of stored product pest control, fumigation being a no residual chemical treatment has remained the mainstay for control of stored product pests. Therefore, it is accepted that fumigation is the most universal and the less hazardous method for maintaining of agricultural products under storage conditions (Keita et al., 2001).

Frequently products are packed in jute bags or plastic bags. Since penetration of the fumigant into the bags is a critical factor it is evident that fumigations under tarps or plastic sheeting should take into account the properties of the packaging materials. For controlling the insect pests by fumigants, the gas must penetrate from the air-space beneath the tarps into the bags containing the stored products. The passage of gas through these polymers to lower layers for eradicating the contamination into packaged foodstuffs is one of the other goals of storage in long-times. Polymers with various thicknesses have different permeability to fumigants (Stout, 1983; Appert, 1987; ACIAR, 1989; Iqbal et al., 1993; Valentini, 1997; Hall, 1970; Marouf & Momen, 2004) (Table 4). So, determining the best thickness of polymer is important in packaging for controlling pests. By incomplete fumigation; specially quarantine pests into packagings can easily enter countries within packaged products. In certain cases such as dried fruit, which are packed in plastic bags, entrance of fumigant into the bags is critical in controlling stored-product insect pests that

originate in the field. Some studies are evident that polypropylene liners of less than 100µm thickness are suitable as inner liners of jute bags to allow the fumigant to enter the bags (because of their high permeability) (Fleural - Lessard & Serrano, 1990; Sedlacek, 2001).

| CO2 gas insecs`s penetration in polymeric packagings (Average±SE) | | | | | | | | |
|---|--------------|------------------|-----------------|-------------------|--------------------|------------|---------------|------------|
| Polymer | Polyethylene | | Cellophane | | Polyvinyl chloride | | Polypropylene | |
| | 16.5 | 29 | 16.5 | 29 | 16.5 | 29 | 16.5 | 29 |
| Thickness (µm) | 1.3±0.013 | 0.44 ± 0.004 | 1.28 ± 0.01 | 0.443 ± 0.005 | 0.4±0.012 | 0.23±0.004 | 0.73±0.004 | 0.32±0.007 |
| (µm) | а | b | a | с | d | f | c | e |
| Table 1 Th | | H | | ermeability | | r | 2 035 | C |

Table 4. The tested polymers to mean permeability the polymers to CO2 gas

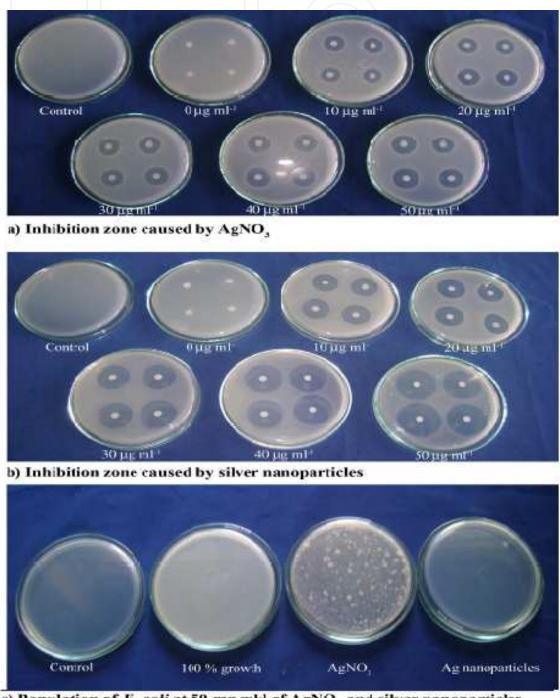
4.2.2 Antimicrobial polymers

The subject is covalently bonding anti-microbial agents to the surface of a selected polymer and its method of use as an anti-microbial agent to reduce surface bacterial, fungus, and/or virus count of the material it contacts (Jo et al., 2009). This can be applied to a variety of applications such as film and container packaging of foodstuffs, cosmetics, medical equipment and devices, environmental, hygienic and sanitary applications, as well as other consumer and commercial use (Kenaway et al., 2007). So, the applied polymers for packaging should be have the ability of coating to materials like nano metals such as silver nanoparticles to gain antimicrobial properties because in usual conditions, there is much growth of microbe agents on packaging polymers (Fig. 2).

Edible coatings have long been known to protect perishable food products from deterioration by retarding dehydration, suppressing respiration, improving textural quality, helping retain volatile flavor compounds and reducing microbial growth (Debeaufort et al., 1998). Specially formulated edible coatings may provide additional protection against contamination of microorganism while serving the similar effect as modified atmosphere storage in modifying internal gas composition (Park, 1999). Among noble-metal nanomaterials, silver nanoparticles have received considerable attentions due to their attractive physicochemical properties. It is well known that silver in various chemical forms has strong toxicity to a wide range of microorganisms (Liau et al., 1997). The larger surface area of silver nanoparticles can improve their antibacterial effectiveness against 150 types of microbes. Although the coating has been extensively studied to increase the shelf life of many agricultural products, little information is available regarding the application of silver nanoparticles-polymers coating for these products.

On the other hand, antimicrobial Polymers, known as polymeric biocides, are a class of polymers with antimicrobial activity, or the ability to inhibit the growth of microorganisms such as bacteria, fungi or protozoans (Fig. 3). In this figure, normal bacterial membranes (panel a) are stabilized by Ca+2 ions binding anionic charged phospholipids. NIMBUS™ quatpolymer rapidly displaces Ca+2 (panel b) leading to loss of fluidity (panel c) and eventual phase separation of different lipids. Domains in the membrane then undergo a transition to smaller micelles. These polymers have been engineered to mimic antimicrobial peptides which are used by the immune systems of living things to kill bacteria. Typically, antimicrobial polymers are produced by attaching or inserting an active antimicrobial agent onto a polymer

backbone via an alkyl or acetyl linker. Antimicrobial polymers may enhance the efficiency and selectivity of currently used antimicrobial agents, while decreasing associated environmental hazards because antimicrobial polymers are generally nonvolatile and chemically stable. This makes this material a prime candidate for use in areas of medicine as a means to fight infection, in the food industry to prevent bacterial contamination, and in water sanitation to inhibit the growth of microorganisms in drinking water (Pyatenko et al., 2004).



c) Population of E. coli at 50 mg ml⁻¹ of AgNO, and silver nanoparticles

Fig. 2. Comparison of E.coli growth inhibition by AgNO3 and silver nanoparticles (Parameswari et al., 2010)

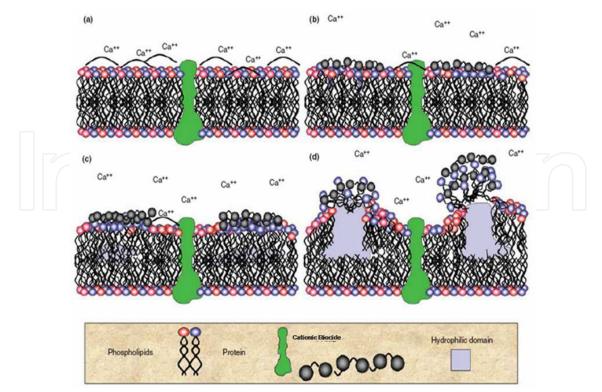


Fig. 3. Action of polymeric cationic biocidal agent (Gilbert and Moore, 2005)

4.2.3 Edible films and coatings

An edible film or coating is simply defined as thin continuous layer of edible material formed on, placed on or between foods or food components (Torres, 1994). Edible packaging refers to the use of edible films, coatings, pouches, bags and other containers as a means of ensuring the safe delivery of food product to the consumer in a sound condition (McHugh & Krochta, 1994). These films can also act as carrier of antioxidant, flavour and bacteriostats and can improve mechanical integrity of food products (Pathania, 2000). Since, package is an integral part of the whole food product, therefore, the composition of the edible packaging must meet with the following specific functional requirements:

- Neutral organoleptic properties (clear, transparent, odourless, tasteless etc.)
- Water vapour tightness to prevent desiccation.
- Good barrier against microbial invasion to reduce spoilage and decay.
- Predetermined permeability to water vapour, O₂ and CO₂ to have complete control over the water and gas exchanges between the product and surrounding atmosphere.
- Good mechanical characteristics (like tensile and yield strength, Spencer impact elongation, etc.) to impart abuse resistence.
- Enchance the surface appearance (e.g. brilliance) and tactile characteristics (e.g. reduced stickiness) of foods (Kaushik, 1999).

4.2.4 Nanotechnology applications in foodstuffs packaging polymers

The development of nanodevices and nanomaterials could open up novel applications in agriculture (Scrinis & Lyons, 2007). Nanophasic and nanostructured materials are attracting

a great deal of attention because of their potential for achieving specific processes and selectivity, especially in biological and pharmaceutical applications (Pal et al., 2007). Nanotechnology derived food packaging materials are the largest category of current nanotechnology applications for the food sector. The main applications for food contact materials (FCMs) including:

- 1. FCMs incorporating nanomaterials to improve packaging properties (flexibility, gas barrier properties, temperature/moisture stability).
- 2. "Active" FCMs that incorporate nanoparticles with antimicrobial or oxygen scavenging properties.
- 3. "Intelligent" food packaging incorporating nanosensors to monitor and report the condition of the food.
- 4. Biodegradable polymer-nanomaterial composites (Chaudhry et al., 2008).

Polymer composites are mixtures of polymers with inorganic or organic fillers with certain geometries (fibers, flakes, spheres, particulates). The use of fillers which have at least one dimension in the nanometric range (nanoparticles) produces polymer nanocomposites. Three types of fillers can be distinguished, depending on how many dimensions are in the nanometric range. Isodimensional nanoparticles, such as spherical silica nanoparticles or semiconductor nanoclusters, have three nanometric dimensions. Nanotubes or whiskers are elongated structures in which two dimensions are in the nanometer scale and the third is larger. When only one dimension is in the nanometer range, the composites are known as polymer-layered crystal nanocomposites, almost exclusively obtained by the intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of layered host crystals (Azeredo, 2009). There are three common methods used to process nanocomposites: solution method, in situ or interlamellar polymerization technique, and melt processing. The solution method can be used to formboth intercalated and exfoliated nanocomposite materials. In the solution method, the nanocomposite clay is first swollen in a solvent. Next, it is added to a polymer solution, and polymer molecules are allowed to extend between the layers of filler. The solvent is then allowed to evaporate. The *in situ* or interlamellar method swells the fillers by absorption of a liquid monomer. After the monomer has penetrated in between the layers of silicates, polymerization is initiated by heat, radiation, or incorporation of an initiator. The melt method is the most commonly used method due to the lack of solvents. In melt processing, the nanocomposite filler is incorporated into a molten polymer and then formed into the final material (Brody et al., 2008). The results of tests performed by An and colleagues (2008) shown in Fig. 4 revealed the evidence for the formation of silver nanoparticles in the coating solutions prepared under the experimental condition. The solutions with PVP formed a thin coating on the surface of asparagus when water evaporated, leaving the nanoparticles evenly distributed in the coating matrix (Jianshen et al., 2008).

Nanocomposite packages are predicted to make up a significant portion of the food packaging market in the near future. Silver is well known for its strong toxicity to a wide range of microorganisms (Liau et al., 1997), besides some processing advantages such as high temperature stability and low volatility (Kumar & Münstedt, 2005). Silver nanoparticles have been shown to be effective antimicrobials (Aymonier et al., 2002; Sondi & Salopek-Sondi, 2004; Son et al., 2006; Yu et al., 2007; Tankhiwale & Bajpai, 2009), even more effective than larger silver particles, thanks to their larger surface area available for

interaction with microbial cells (An et al., 2008; Kvítek et al., 2008). In fact, the most common nanocomposites used as antimicrobial films for food packaging are based on silver nanoparticles, whose antimicrobial activity has been ascribed to different mechanisms, namely: (a) adhesion to the cell surface, degradation of lipopolysaccharides and formation of "pits" in the membranes, largely increasing permeability (Sondi & Salopek-Sondi, 2004); (b) penetration inside bacterial cell, damaging DNA (Li et al., 2008); and (c) releasing antimicrobial Ag+ ions by dissolution of silver nanoparticles (Morones et al., 2005). The latter mechanism is consistent with findings by Kumar & Münstedt (2005), who have concluded that the antimicrobial activity of silverbased systems depends on releasing of Ag+, which binds to electron donor groups in biological molecules containing sulphur, oxygen or nitrogen. Besides the antimicrobial activity, silver nanoparticles have been reported to absorb and decompose ethylene, which may contribute to their effects on extending shelf life of fruits and vegetables (Li et al., 2009).

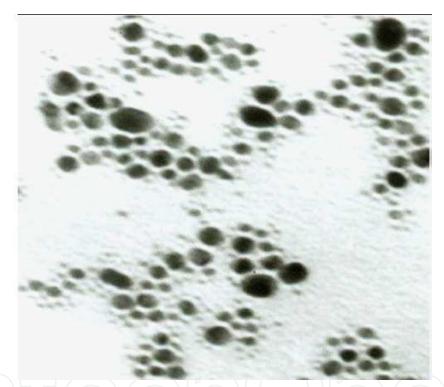


Fig. 4. Transmission electron microscopy (TEM) of silver nanoparticles (×100,000) (An et al, 2008)

5. Suitable polymer for stored-product packaging

Plastics based on Polypropylene, Polyethylene, Polyvinyl Chloride and Cellophane, hugely used for packagings, has some of these properties but this is different at them. For example, these polymers rank generally from the easiest to the most difficult to penetration against insect pests; Cellophane, polyethylene, Polyvinylchloride and Polypropylene. The least penetration is carried out in PP and PVC polymers. Foodstuffs packaged by polymer films of PP and PVC could provide the conditions and so, by suitable packaging the stored pest insects do not access to food and without food they become extinct. But in the comparison between polypropylene and polyvinylchloride, PVC isn't a safe polymer for packaging

foodstuffs in order to release HCl gas and the only importance of PVC in storage industry is often to be used as a gas-tight cover on agricultural products to keep a suitable concentration of gas and it is important for controlling quarantine pests. Furthermore, other two polymers, Polyethylene and Cellophane have a high permeability to gases but a very low resistance to pests as the product packaged into them becomes more contamination than ones into PVC and PP. The polymer films of Polyethylene and Cellophane; specially Cellophane, is greatly used for packaging the products be consumed daily. Moreover, Cellophane is 100% biodegradable. Some studies show that polypropylene had a good degradability in environment in comparative to polyethylene and polyvinylchloride. Also, new studies show that polypropylene has a suitable property for coating with nano metals and repellents for decreasing the losses of stored-products in effect of pest infestation. Hence, according to the investigations of researchers (in above) polypropylene usually is used as a suitable cover for packaging foodstuffs in stores and has perfect physical and chemical properties for the packaging works which should be performed in stores of maintaining foodstuffs.

6. Polypropylene as packaging polymer

PP known as polypropene, is one of those most versatile polymers available with applications, both as a plastic and as a fibre, in virtually all of the plastics end-use markets. Professor Giulio Natta produced the first polypropylene resin in Spain in 1954. Natta utilised catalysts developed for the polyethylene industry and applied the technology to propylene gas. Commercial production began in 1957 and polypropylene usage has displayed strong growth from this date. PP is a linear hydrocarbon polymer, expressed as

| | Polypropylene | | |
|---|--|--|--|
| | IUPAC name poly(propene) Other names | | |
| Polipropene 2 | opylene; Polypropene; 5 [USAN];Propene polymers; ne polymers; 1-Propene | | |
| | Identifiers | | |
| CAS number 9003-07-0 | | | |
| | Properties | | |
| Molecular formula | (C3H6) _n | | |
| Density 0.855 g/cm3, amorphous 0.946 g/cm3, crystalline | | | |
| Melting point 130–171°C | | | |
| Except where noted otherwise | nat is this?) (verify) , data are given for materials in their standard e (at 25°C, 100 kPa) | | |

16

 C_nH_{2n} . PP, like polyethylene (see HDPE, L/LLDPE) and polybutene (PB), is a polyolefin or saturated polymer. (Semi-rigid, translucent, good chemical resistance, tough, good fatigue resistance, integral hinge property, good heat resistance). PP does not present stress-cracking problems and offers excellent electrical and chemical resistance at higher temperatures. While the properties of PP are similar to those of Polyethylene, there are specific differences. These include a lower density, higher softening point (PP doesn't melt below 160°C, Polyethylene, a more common plastic, will anneal at around 100°C) and higher rigidity and hardness (Cacciari, 1993). Additives are applied to all commercially produced polypropylene resins to protect the polymer during processing and to enhance end-use performance. PP is a thermoplastic which is commonly used for plastic moldings, stationary folders, packaging materials, plastic tubs, non-absorbable sutures, diapers etc. PP can be degraded when it is exposed to ultraviolet radiation from sunlight. Furthermore, at high temperatures, PP is oxidized. The possibility of degrading PP with microorganisms has been investigated.

Three main types of PP polymer types are used in household packaging:

- 1. Homopolymer PP: this is a translucent polymer, with high Heat Distortion Temperature (HDT), with a lower impact strength (particularly at low temperatures) and is used for applications such as closures and soup pots;
- 2. Block copolymer PP: this polymer has a lower transparency and generally a lower HDT, with a higher impact strength (particularly at low temperatures) and is used for applications such as ice cream containers and for chilled foods;
- 3. Random copolymer PP: this polymer has a high transparency and the lowest HDT. It is a product with the greatest flexibility and possesses reasonable impact strength. Typical applications requiring high transparency are bottles and salad bowls; Homopolymer and copolymer (random and block) PP polymer types may be used with either of the two main types of moulding process (extrusion/thermoforming or extrusion blow moulding) and therefore can be made with different melt flow characteristics as follows:
- 4. Thermoforming and blow moulding: used for meat trays and bottles, with a low MFR (Melt Flow Rate) (1 to 4);
- 5. Injection moulding: used for thin walled packaging, such as soup pots, with a high MFR (33 and higher).

Thus, Polypropylene is a thermoplastic polymer used in a wide variety of applications including packaging, textiles (e.g. ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. An addition polymer made from the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids. The versatility of the polymer (the ability to adapt to a wide range of fabrication methods and applications) has sustained growth rates enabling PP to challenge the market share of a host of alternative materials in plethora of applications. In 2007, the global market for polypropylene had a volume of 45.1 million tons, which led to a turnover of about 65 billion US-dollars (47.4 billion Euro) (Kenaway et al., 2007). PP films are used in household paper packing, stationery packaging, portfolios and food packaging. In stationer industry, they are used for photo albums and page protectors. PP films are used as a lamination layer, both as sealant and as heat resistant layer and in the pressure sensitive industry for adhesive coating and diaper closures. Various packaging of products could be made of this film.

7. Conclusion

According to the results of performed works in the field of packaging, it is proved that a polymeric cover usually made of polypropylene with thickness <100 µm is the most suitable one for foodstuffs packaging. In the less thickness, some polymers have less resistant to the infestation of pest insects although polypropylene shows resistance well ever in lower thicknesses. Such cover would undoubtedly reduce the danger of crossinfestation and on the one hand, propylene is permeable to stored gases such as phosphine for ruining the contaminations into stored products and has the ability of coating to nano metals in the thickness and thus could obtain the antimicrobial properties. Also, propylene has a good degradability among polyolefines. A consultation exercise with the PP packaging supply chain explored the levels of interest of using a food grade PP in packaging applications. Little recycled PP is currently used in packaging because little is currently available. There is certainly interest from all levels of the supply chain - retailers, brand owners, food manufacturers and packaging manufacturers - in using recycled PP, if a recycling system existed that could meet regulatory standards and company food performance standards (Anonymous, 2010). Such a change would undoubtedly reduce the too using of chemical pesticides and increase the storages food maintaining and therefore reduce economic losses associated with infestation and minimize injury to company image as a manufacture of high quality foodstuffs.

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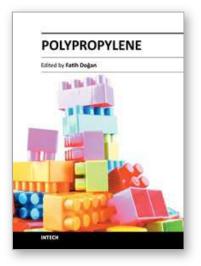
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Polypropylene Edited by Dr. Fatih Dogan

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This book aims to bring together researchers and their papers on polypropylene, and to describe and illustrate the developmental stages polypropylene has gone through over the last 70 years. Besides, one can find papers not only on every application and practice of polypropylene but also on the latest polypropylene technologies. It is also intended in this compilation to present information on polypropylene in a medium readily accessible for any reader.

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University Campus STeP Ri Slavka Krautzeka 83/A 51000 Rijeka, Croatia Phone: +385 (51) 770 447 Fax: +385 (51) 686 166 www.intechopen.com

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