

FEDERAL UNIVERSITY OF TECHNOLOGY
DEPARTMENT OF FOOD SCIENCE AND
TECHNOLOGY
FST 511
(FOOD PACKAGING)

Packaging has been defined as a socio-scientific discipline which operates in society to ensure delivery of goods to the ultimate consumer in the best condition intended for their use. Also it can be defined as a co-ordinated system of preparing goods for transport, distribution, storage, retailing and end-use, a means of ensuring safe delivery to the ultimate consumer in sound condition optimizing cost of delivery while maximizing sales.

It is important to distinguish between the words "package", "packaging" and "packing".

The package is the physical entity that contains the product

Packing is the enclosing of an individual item or several items in a package or container.

However, there are 4 levels of packages.

- a) **Primary package:** This is one which is in direct contact with the contained product. It provides the initial and usually the major protective barriers e.g. are metal cans, paperboard cartons, glass bottles and plastics pouches.
- b) **Secondary package:** A secondary package contains a number of primary packages. It is the physical distribution carrier and is sometimes designed so that it can be used in retail outlets for the display of primary packages. E.g. a carton of evaporated milk.
- c) **Tertiary package:** The package is made up of number of secondary packages e.g. a carton of sweets.
- d) The 4th level: **Quaternary package** is frequently used to facilitate the handling of tertiary packages. This is generally a metal container up to 40m in length which can hold many tertiary packages when being transferred to or from ships, trains and flatbed trucks by giant cranes.

Functions of Packaging

- 1) Packages serve as containers which will permit safe transfer of food from one place to the other until it reaches the ultimate consumer



- 2) Protects the food from spoilage due to microbial action, damage by insects, rodents and other pests.
- 3) Protect the food from deterioration due to environmental factors like moisture, light oxygen etc.
- 4) Promote the development of quality during ageing or maturation
- 5) It promotes convenience in the use of foods
- 6) Prevents the transmission of foreign odours to the food or loss of aroma from the food
- 7) It serves as a vehicle through which the producer communicates to the consumer as well as vehicle for promotion and advertisement
- 8) Serves as a utensil for retention and serving of foods.

PACKAGE ENVIRONMENTS

The packaging aims to perform its function in three different environments and failure to consider these environments during package development of any particular food can result to poorly designed package, increased costs, consumer complaints and even avoidance or rejection of the product by the customer.

- a) **Physical Environment:** This is the environment in which physical damage can be caused to the product. It includes shocks from drops, falls and bumps, damage from vibrations arising from transportation modes including road, rail, sea and air and compression and crushing damage arising from stacking during transportation or storage in warehouses, retail outlets and the home environment.
- b) **Ambient Environment:** The environment which surrounds the package. Damage to the product can be caused as a result of gases (particularly O_2) water and water vapor, light (particularly UV) and temperatures, as well as micro-organisms (bacteria, fungi, molds, yeasts and viruses) and macro-organisms (rodents, insects, mites and birds) which are everywhere in warehouses, retail outlets. Exhaust fumes from automobiles, dust and dirt can also gain entry into the package unless the package acts as an effective barrier.
- c) **Human Environment:** This is the environment in which the package interacts with people and designing packages for this environment requires knowledge of the variability of consumer's capabilities in vision, strength, weakness, memory and cognitive behaviour. Since one of the functions of the package is to communicate, it is important that the messages on them are clearly received by consumers and the labeling done accordingly to the standard stipulated by the law.

GLASS PACKAGING MATERIALS

Glass is an amorphous inorganic product of fusion that has been cooled to a rapid condition without crystallization. Although glass is often regarded as synthetic material, it was formed naturally from common elements in the earth's crust. Natural occurring materials such as "obsidian" (from magma or molten igneous rock) and tektites (from meteors) have compositions and properties similar to those of synthetic glass. pumice is a naturally occurring foam glass. Although the origin of the first synthetic glasses is lost in history, the first glass vessel was discovered in about 3000 BC. The techniques for glass making ranges from pouring of molten glass or winding glass threads over a sand mold to the use of blowing iron which is a tube to which red-hot, highly malleable glass adheres. Blowing through one end of the iron causes the viscous liquid to balloon at the other end, leading to the production of hollow glass objects.

By 200AD, articles of glass were in fairly common use in Roman households and by the following 1000 years, glassmaking techniques have spread over Europe. Further developments have occurred resulting in the production of a wide range of glass containers for packaging. The two main types of glass container used in food packaging are bottles and jars.

COMPOSITION OF GLASS

The basic raw materials for glassmaking come from mines or quarries and must be smelted or chemically reduced to their oxides at temp exceeding 1500°C . The principal ingredient of glass is silicon derived from sand, flint or quartz. Silica can be melted at temp of about 1723°C to form fused silica glass which, because of its high melting point is used for specialized applications like laboratory glasses.

Usually silica is combined with other raw materials in various proportions to produce glass wares with specialized characteristics. Sodium and potassium carbonates (alkali fluxes) are usually added to silica in glassmaking in order to lower the fusion temperature and its viscosity.

Ca and Mg carbonates (limestone and dolomite) are usually added as stabilizers which prevents the glass from dissolving in water. Other ingredients added to give glass certain physical properties include lead which gives clarity and brilliance although at the expense of softness of the glass. Alumina increases hardness and durability. Addition of about 6% boron to form borosilicate glass reduces the leaching of sodium from the glass into the water.

As a consequence of sodium in glass being loosely combined in the silica matrix as a result of the addition of sodium or potassium carbonate to reduce the fusion temperature, the glass surface is subject to 3 forms of corrosion, etching, leaching and weathering.

Etching is characterized by alkali attack which slowly destroys the silica network, releasing other components of the glass.

Leaching is characterized by acid attack in which hydrogen ions exchange for alkali or other positively charged mobile ions. The remaining glass principally silica usually retains its mortal integrity.

Weathering is not really a problem in commercial glass packaging application since it may take centuries to become apparent. However, a mild form of weathering is commonly known as surface bloom and may occur under extended storage period.

The most aggressive solution on glass is double-distilled water at neutral pH 7. The effect of dilute acidic solutions is much less, the main action being the extraction of sodium ions, which are replaced by hydrogen ions. The result is a surface zone where the glass is depleted of sodium, this dealcalized layer forming a barrier to further ionic diffusion. It is worth noting that the aqueous phase of almost all food products is acidic.

MANUFACTURING OF GLASS

Most of the glass we see around us in our everyday lives in the form of bottles, jars or drinking glasses is known as commercial glass or soda-lime glass. A typical composition of commercial glass is silica (SiO_2) 68 – 73%, calcia (CaO) 10 – 13%, soda (Na_2O) 12 – 15%, alumina (Al_2O_3) 1.5 – 2% and iron oxides (FeO) 0.05 – 0.25%, depending on the glassmaker and the raw materials being used.

From the composition given above, the largest constituent (68 – 73%) is silica; the second largest constituent (15 – 50%) is cullet (scrap or recycled glass), originating as both glass scrap from the factory and recycled glass from consumers. Although the use of cullet can cause problems with the production of some types of glass unless there is good separation of coloured glass and removal of associated materials such as labels. The use of cullets is economically desirable since less energy is required to melt cullet than new raw materials. Cullet also reduce the amount of dust and other particulate matter that often accompanies a batch made exclusively from new raw materials.

The manufacturing of glass involves the following

- a) Mixing and melting
- b) Forming process
- c) Annealing
- d) Surface treatments

Mixing and melting

The raw materials are weighed, mixed and charged into a glass-melting furnace, which is maintained at a temperature of approximately 1500°C . Here they are converted into molten glass that is chemically homogenous and virtually free from gaseous inclusion (bubbles). The melting process consists of 2 phases: (1) changing the solids into a liquid and (2) fining or "clearing up" of the liquid. During the refining process, gases (CO_2 , SO_2 and water vapour) produced by the chemical reaction rise to the surface of the furnace and are removed.

When the molten glass becomes free of gas (seed-free), it is then ready for forming into containers. It moves from the furnace into the working end of the furnace where thermal homogenization and cooling of the glass to viscosity required for the particular operation begin. This point, the temperature of the melt has been lowered from $1250 - 1350^{\circ}\text{C}$ to approximately 1100°C .

Forming process

The glass is carried from the working end of the furnace to the forming machine in a channel-like structure called a forehearth, which is fired by a number of small burners, the aim being to ensure uniform temperature distribution throughout the depth of the glass. At the end of the forehearth is a gob-forming mechanism consisting of a rotating sleeve and vertical plunger. The glass exits in a continuous, viscous stream which is cut by rapidly moving, horizontal steel blades to form what is known as a gob (lump or mass of molten glass).

The process of converting a cylindrically shaped gob of glass into a bottle or jar is called forming and it is essentially a controlled cooling process using a molding or forming machine which performs 2 basic functions: shapes the gob into hollow container and simultaneously removes heat from the gob to prevent it from deforming significantly under its own weight.

Two basic types of processes used in the forming of glass containers are (B & B) i.e. Blow and Blow process and the second (P & B) i.e. Process and Blow process. B & B for glass bottles while P & B for glass jars.

Blow and Blow process

Annealing

After forming, the glass containers, they are transferred to annealing oven where they are heated to a temperature of approximately 540°C , held at this temp for few minutes and then cooled at a uniform rate to produce a stable product by removal of any residual stress resulting from non uniform cooling rates during forming and handling.

Surface treatments

The strength of a newly made glass container can be rapidly reduced by moisture or abrasion, and some form of surface treatments to increase the strength is essential. Two types of surface treatment are applied to glass containers in order to modify their mechanical properties.

1) Hot-End Treatment

This is typically carried out while the glass container is at 550°C . Here vapor containing tin or titanium generally in the form of tetrachloride is brought into contact with the outside of the container to form a thin unimolecular film of metal oxide. This treatment prevents surface damage while the container is still hot, strengthens the surface and improves the adhesion of the subsequent cold-end coating.

2) Cold-End Treatment

This is carried out while the temp of the glass container is $>100^{\circ}\text{C}$. It is designed to protect the container surface and assist its flow through the filling line. It involves spraying an organic material in an aqueous base containing either waxes, stearates, silicones or oleic acid or polyethylene on the outside of the container to increase its lubricating by providing a surface with a low coefficient of friction.

3) Shrink Sleeves

In shrink sleeves treatments, 2 types of protective materials are used. One is made from thin foamed PS, the other is made from PVC or PS. The former offers some thermal insulation to the container while the latter which usually wraps the bottle from its neck to the underneath helps to contain the fragments and prevents shattered glass being scattered in all direction if the bottle is dropped.

Characteristics of glass packaging material

Glass has remained an important packaging material because of such peculiar characteristics as

- **Chemical inertness:** Glass exhibits a high degree of resistance to chemical attack except hydrofluoric acid which attacks it appreciably. However, the degree of inertness is influenced by chemical composition of the glass in other words; some are more chemically inert than others.

Also time and temp of the attacking reagent as well as contact with other hazardous element. It is however known that neutral glasses are more resistant to chemical attack than alkaline glasses.

- **Non-permeability:** Glass is impermeable to all glasses, solutions and solvents. This is about the strongest characteristic that makes glass the choicest of all packaging materials. It makes it very suitable for packaging hygroscopic products. It also preserves delicate volatile flavours.
- **Strength:** The strength of a glass container varies with the type and condition of the surface. Tempered glass (annealed) has greater tensile strength. Smooth surface glasses have high strength and scratches and bruises on glass surfaces give raise to appreciable reduction in tensile strength. These scratches and imperfections act as stress concentrators and glass failure or fractures often start from these points on the surfaces and continue outward. The strength and rigidity of glass containers lead them to high vertical stacking.
- **Resistance to high internal pressure:** Glass is able to withstand high internal pressures as well as external one and this is because of its high rigidity and strength. It is heat resistant and has high melting point thus it is ideal for both moist and dry sterilization.
- **Optical Properties:** The high degree of transparency of glass provides appetite exciting appeal to products. The opaque or amber coloured containers provide appreciable protection to light sensitive products. However, the degree of protection varies with the extent to which the glass excludes light to the product and the radiation to which the product is sensitive to. Amber coloured glass excludes light below 450nm while green glass excludes light of about 350nm wavelengths.
- **Surface smoothness:** This characteristic makes cleaning easy. This also impacts some degree of brilliance to the packaged product which is an asset in marketing of the product.

Disadvantages of glass materials

- 1) **Weight:** It is heavier than most packaging materials thus posing a problem in transportation and handling.
- 2) **Fragility:** Glass materials are generally fragile and so are highly susceptible to breakage leading to loss of the packaged product.
- 3) **Expense:** It is more costly than many of the other packaging materials thus resulting to high cost of production.

METAL PACKAGING MATERIAL

Four metals are commonly used for the packaging of foods: steel, aluminum, tin and chromium. Tin coated on steel, chromium on steel are used as composite materials in the form of tin plate and electrolytically chromium-coated steel (ECCs) with the later referred to as tin-free steel (TFS). Aluminium is used in the form of purified alloys containing small and carefully controlled amounts of magnesium and manganese. Two other metals used in metal packaging are lead and copper but are used as soldering or welding materials in three-piece tinfoil and ECCS containers.

Manufacture of Tinfoil

The term tinfoil refers to low carbon mild steel sheet varying in thickness from around 0.15 to 0.5mm with a coating of tin between 2.8 – 19 gram per square meter (gm^{-2}) (0.4 – 2.5 μm thick), on each surface of the materials. The combination of tin and steel produces a material that has good strength combined with excellent fabrication qualities such as ductility, drawability as well as good solderability, weldability, non toxicity, lubricity, lacquerability and a corrosion-resistant surface of bright appearance. Furthermore, the tin coating adheres sufficiently to the steel base so that it will withstand any degree of deformation that the steel is able to withstand without flaking.

Tinplating

The traditional method of tinplating involves dipping or passing the steel through a bath of molten pure tin but this has been replaced since the introduction of electroplating process which enables different thickness of tin to be applied to the two surfaces of the steel. This differential tinplate is of economic benefit to the user because it enables the most cost effective coating to be selected to withstand the different conditions of the interior and exterior of the container.

There are a number of methods of electroplating but the 2 principal methods are acid stannous sulfate process and halogen process. Plating by either of this method is preceded by cleaning in a pickling and degreasing unit, followed by thorough washing to prepare the surface for plating. After the plating which is done by electroplating, the coating is flow melted, passivated and then lightly oiled.

Flow melting consists of heating the strip to a temperature above the melting point of tin ($260 - 270^{\circ}\text{C}$) followed by rapid quenching in water. During this treatment, a small quantity of the tin-iron compound FeSn_2 is formed; the weight and structure of which depends on the time and temperature as well as other factors such as the surface condition of the steel. The structure and weight of this alloy plays an important role in several forms of corrosion behaviour. But because the naturally formed layer on the surface of the tin will readily grow in the atmosphere to form a yellow stain especially when heated, the steel strip is given a passivation treatment to render its surface more stable and resistant to the atmosphere. This involves an electrolytic treatment in sodium dichromate electrolyte to form a film consisting of chromium and chromium oxide and tin oxides, the quantity and form determining the varying degree of properties of the film.

After passivation, the plate is given a light oiling ($5 - 10\text{mgm}^{-2}$) to help preserve it from attack and to assist the passage of the sheets through container-forming machines without damaging the soft tin layer. It is essential that the oil used is permissible for use in food packaging e.g. is cotton seed oil or dioctylsebacate and acetyl tributyl citrate.

The final structure of the completed coating is shown below.

Types of steel produced for subsequent use as tinplate

Composition % (maximum)

Type	C	Mn	P	S	Si	Cu	Application
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I	0.13	0.60	0.015	0.05	0.01	0.06	Used where high internal corrosive resistance is required e.g. high acid food e.g. fruit juice
MR	0.13	0.60	0.02	0.05	0.01	0.20	Where internal corrosion resistance is not too critical e.g. mild acid foods vegetables
N	0.13	0.060	0.015	0.05	0.01	0.06	Used where high strength and rigidity is required e.g. can ends
D	0.12	0.60	0.02	0.05	0.02	0.20	Used for severe drawing operations

* Enamel or Lacquer

To effect further protection and diversify packaging application, enamels or lacquer might be applied to the tin coating or to the tinless steel base plate.

Among the materials used as enamels are plastics, resins, glass and inorganic oxides. By varying the chemical composition and combinations of the materials, various specific packaging material requirements can be met. There are 2 major types of can enamel used in food package:

- 1) The acid resisting lacquer which is used for can meant for high coloured foods
- 2) The sulphur reacting lacquer used in cans for vegetables like corns, beans, peas and meat products which contain very little acid but high quantity of sulphides from the denaturation of sulphur amino acids during heat processing. The sulphides produced through harmless react with Fe and Cu contained in the food to produce dark coloured Fe or Cu sulphide. To prevent this, the cans are coated with lacquer containing zinc oxide. The zinc oxide reacts with the sulphide from the food to form a colourless zinc sulphide thus preventing the formation of dark coloured iron or copper sulphide on the product.

Characteristics of enamel coating lacquer

- 1) It must impart no colour or flavor to the food
- 2) It must be acceptable for contact with food under the food additive amendment program
- 3) It must protect the can and content during the required shelf life
- 4) It must not flake off the plate during can manufacture or in subsequent storage
- 5) It must be nominal in cost, easy to apply and quickly cured
- 6) It must withstand all temperature encountered during processing and normal storage.

Aluminum

Aluminum is the earth's most abundant metallic constituent comprising 8.8% of the earth's crust with only the nonmetals O_2 and silicon being more abundant. Aluminum oxide is the only oxide formed by aluminum and is found in nature in different types as corundum (Al_2O_3), diaspore ($Al_2O_3 \cdot H_2O$), gibbsite ($Al_2O_3 \cdot 3H_2O$).

Currently, aluminum is produced by dissolving the aluminum oxides in cryolite in carbon-lined steel boxes called pots. A carbon electrode or anode is lowered into the solution and an electric current of 50 – 150 MA is passed through the mixture to the carbon cathode to produce O_2 which combine with the anode's carbon to form CO_2 while the aluminum settles to the bottom of the pot.

Most commercial uses of aluminum require properties that the pure metal cannot provide thus alloying with some other metals help to improve the impart strength, improve formability characteristic and influence corrosion characteristics of aluminum.

What is sanitary can?

Sanitary cans have also been fabricated from aluminum and these have made substantial impact in the beer and carbonated drink industry. Aluminum has a lot of advantages over tin cans

- 1) It is lighter in weight and this property ensures reduced transportation cost.
- 2) It is non toxic and this can be used in direct contact with foods
- 3) It does not form sulphidediscolouration
- 4) It is corrosion resistant; due to aluminum oxide form which is responsible to its resistance to atmospheric corrosion but inside the can where there is depletion of this oxide, the aluminum is no longer resistant and coating with enamel or lacquer will help to resistant corrosion
- 5) Aluminum is easy to fold to varying shapes. It can extruded or rolled to varying thin sheets.
- 6) Aluminum has higher heat conductivity than other packaging materials therefore permitting faster freezing and heating operations
- 7) Aluminum is impermeable to moisture vapour and gases and gas resistance and low water vapour transmission rate is an important requirement in the choice of packaging material
- 8) It has high reflectivity which provides appreciable insulation value and eye appeal. Coatings lower the reflective value by absorbing some of the incident rays. The low emission characteristics of this metal is used to an advantage in Al foil used in cook-in or heat-in packages of prepared foods. In such foods, it is desired or required that minimum heat be lost before serving. A major disadvantage of Al is the low strength. Al has much less strength than tin plate of the same thickness. However, this soft and ductility problems are averted by alloying with Mn to attain higher tensile strength but this has an adverse effect on its resistance to corrosion.
- 9) Aluminum also very expensive

Metal foils

Metals like Al, Pb and tin have been used for production of metal foils. But the most important and commonly used is Al. such characteristics as lightness in weight, strength and compatibility with many products make Al the choice metal for foil. They are used in thickness that range from 0.000025 – 0.0025 inch and for the uncoated foil, the thickness determines its protective properties. Foils of low thickness have microscopic pores or pin holes and so allow limited diffusion of gases and water vapour.

Foils of such low thickness can be improved in quantity by coating with enamels or plastics.

Plastics

These are synthetic or man-made materials produced by the application of heat and pressure on some polymers (resins) which can then be formed into useful objects. The resins or binder is the essential and central constituent of plastics and it is obtained from either plants or from petroleum refining process as intermediate products.

Resins from vegetable matter can be obtained from cellulose from cotton, furfural from oat hulls, oil from seeds and various starch derivatives.

Plastics is obtained from petroleum following the sequence.

- a) Drilling and transportation of petroleum to refinery
- b) Crude oil or natural gas is refined into ethane, propane and hundreds of petrochemical products of which fuel and kerosene are inclusive.
- c) Ethane and propane are converted to ethylene and propylene using high-temp furnace
- d) Catalyst is combined with ethylene or propylene to form fluff (polymer) a powdered material resembling laundry detergent
- e) Fluff is combined with additives (filliers, plasticizers, colourants etc.) depending on the type of plastics
- f) Polymer is fed to extruder where it is melted, mixed with the additives and extruded
- g) The melted plastics is cooled and fed into pelletizer where it is cut into small pellets used for molding of plastics into various shapes.

Molding of plastics

Plastics can be molded into different shapes using the following methods

- 1) Extrusion molding: Here a heated plastic mass is forced continuously through a forming die made in the desired shape. The formed plastics cool under blown air or in water bath or harden on a moving belt.

- 2) Injection molding: The plastic is heated to a semifluid state, is squirted into a mold under great pressure and hardens quickly. The mold is then opened and the parts released to produce the plastic molded.
- 3) Blow molding: Here pressure is used to form hollow objects either by direct or indirect method
 - (a) Direct method: A partially shaped heated plastic form is inserted into a mold. Air is blown into the form, forcing the plastic form to expand to the shape of the mold to give the final shape desired
 - (b) Indirect method: A plastic sheet or special shape is heated and clamped between a die and a cover. Air is forced between the plastics and the cover and this presses the material into the shape of the die to give the final shape of the desired shape.

Plastics

These are synthetic or man made materials produced by the application of heat and pressure on some polymers and co-polymers which can then be formed into useful objects. The resin or binder is the essential and central constituent of plastic material. It determines the physical and chemical characteristics of the various members of plastic materials. It is the basic plastic ingredient. It is usually available in forms of powder, flakes, ground and for some purposes liquids.

Plastics vary considerably in chemical constituents and hence properties. The simpler plastics like the clear plastic film contain about 90 – 95% of the basic resin and only small amount of additives. Some other complex ones contain only 20 – 30% of the basic resin and various properties of secondary ingredients such as fillers, plasticizers, colourants, and other miscellaneous additives. Filled plastics are mainly moulded article made from such complex combinations. The characteristics of such plastics are influenced by the secondary ingredients added though the properties can also vary based on the chemical constituents.

Certain characteristics are general to all plastics and these are

- 1) Fabrication adaptability: Most plastics are readily adaptable to mass production methods. It can also be easily made to fit intricate product design and at low production cost. However, some plastic wares of special qualities may be quite expensive particularly when fabricated or procured in small quantities.
- 2) Weight: Plastics have very low density when compared to most packaging materials particularly metals and glass. They therefore offer high weight savings cost. The light weight together with its strength give the material an edge over other packaging materials.
- 3) Corrosion: Most plastics if not all are immuned to rust and corrosion.
- 4) Insulation: Plastics are poor insulators of heat, however, most can be burnt and are susceptible fire hazards.
- 5) Variety: They can be produced in wide range of variety to suit the need in question example plastics can be produced in a wide range of colours suitable for light sensitive products.

- 6) Disposal: Because of its susceptibility to burning, it can be easily disposed of after use by burning.
- 7) Stability: Plastics i.e. thermoplastics are not stable to heat, they may warp, shrink or creep when subjected to heat. They get relatively soft and becomes easy to scratch.
- 8) Odour: Many plastics have definite odours, which may be unpleasant and can be impacted into foods.

• Types of plastics

There are two types of plastics, thermoplastics and thermosetting polymers. Thermoplastics are those plastics that do not undergo any chemical change in their composition when heated and can be moulded again and again by melting under heat and moulding to desired shape. Thermosetting polymers are those that form bond between polymers strands when heated creating a tangled matrix that cannot be undone i.e. the shape cannot be changed without destroying the plastic. They are tough and temperature resistant and can melt to take shape once, after they have solidified, they stay solid.

Over thirty different plastics are used in food packaging but the most common ones are the polyolefins, polyvinyls and polyesters which are all thermoplastic material.

- 1) Common examples of polyolefins are polyethylene and polypropylene.
 - a) Polyethylene: This is available in 3 grades: low, medium and high density polyethylene. The low density accounts for the biggest proportion of these plastics used in packaging because of its versatility. It can be extruded into film, blown into bottles and injection mould, closures and dispensers. Polyethylene has a waxy feel and is relatively inert chemically. It is almost insoluble in all solvents at room temperature but with hydrocarbons and chlorinated hydrocarbons. Some softening and swelling can occur. It is a clear, tough polymer with exceptional gas and moisture barrier properties. PET's ability to contain CO₂ (carbonation) makes it ideal use in soft drink bottles. Examples of PET packages.
 - i) Low density: Low strength and toughness. Retail units films
 - ii) Medium density: Offers clarity and flexibility. It is used to make bottles that require flexibility. To take advantage of its strength and toughness in film form, it is used to produce shopping bags, garbage bags and coating for milk cartons.
 - iii) HDPE: Has very high tensile strength and excellent protective barrier properties. It is used for some water containers (GFI: PEE), some household chemicals and mostly for industrial chemicals and detergents.
 - b) Polypropylene: This is rigid polymer used for fabrication of packages meant to carry load. It has high tensile strength and is similar to polyethylene chemically. It is ideal for use in caps and lids that have to hold

tightly on to threaded openings. Because of its high melting point, polypropylene can be hot-filled with products designed to cool in bottles, including ketchup and syrup. It is also used for products that need to be incubated such as yogurt. Many storage food containers or components are made from PP example bottle caps, take-out food containers and even drinking straws.

2) Polyvinyl (Polyvinyl chloride or PVC): This provides excellent clarity, puncture resistance and cling. Chemically it is resistant to weak and strong acids and alkalines but soluble in esters and ketones. It has moderate barrier to moisture and as a film allows good passage of gases and vapours across it which makes it ideal for packaging of fresh meats that require oxygen to ensure a bright red surface while maintaining an acceptable shelf life. Examples plastic food wrap, shrink wrap etc.

3) Polystyrene (PS)

This is an inert material that is used for different applications. It is resistant to microbial growth and has almost zero water absorption [property. It is light weight and has low thermal conductivity and excellent cushioning property. In its crystalline form, it is a colourless plastic that can be clear and hard. It can be foamed to provide exceptional insulation properties. Foamed or expanded polystyrene is used for products such as meat trays, egg cartoons and coffee cups. It is also used for packaging and protecting appliances of electronics and other sensitive products.

Toxicity

Plastics are insoluble in water and have relative chemical inertness. Pure plastics generally have low toxicity in their finished state and will pass through the digestive system with no ill effect other than mechanical damage or obstruction. However, plastics often contain a variety of toxic additives for example, plasticizers which are often added to brittle plastics like polyvinyl chloride to make them pliable enough for use in food packaging. Traces of these chemicals can leach out of the plastics when it comes into contact with food. Because of this, such plasticizers as di-z-ethylhenyl phthalate mostly used in PVC is banned for use in PVC packages meant for food packaging.

Moreover, while the finished plastic may be non-toxic, the monomers used in its manufacture may be toxic and small amounts of those chemicals may remain trapped in the product. Because of this the WHO International Agency for Research on Cancer has recognized the chemicals used in PVC as a known human carcinogen.

Environmental issues

Plastics are durable and degrade very slowly, the molecular bonds that make plastics so durable also make them equally resistant to natural degradation process. Because of this plastics are usually burnt though releases toxic fumes hazardous to health. Plastic recycling has been the best way of managing plastics waste and can also be broken down to liquid hydrocarbons which serve as raw material for manufacturing of different end uses. However, it can be used in cement plants as a means of generating fuel.

Paper

Paper is a generic term that refers to all materials derived from vegetable or cellulose fibers. It is the oldest packaging material and the most versatile of all packaging materials. The packaging characteristics of paper vary considerably with the process of manufacture and the additional treatments that the finished paper is subjected to. For instance, the strength and mechanical properties of paper usually depend on the mechanical treatment of the cellulose fiber and on the inclusion of fillers and binding agents.

Half of the fiber used for paper today comes from wood that has been purposely harvested for its use. The remaining material comes from wood fiber from wood fiber from sawmills, recycled newspaper, some vegetable matter and recycled cloth. Coniferous trees such as spruce and fir, used to be preferred for papermaking because the cellulose fibers in the pulp of these species are longer, therefore making for stronger paper. These trees are called "softwood" by the paper industry.

Deciduous trees (leafy trees such as popular) are called "hardwood". Because of increasing demand for paper and improvements in pulp processing technology, almost any specie of tree can now be used for paper. However, some plants other than trees are suitable for paper-making. In areas without significant forests, bamboo, straw and even sugarcane can be used for paper.

The manufacturing process

- a) Making of pulp: The first stage in manufacturing of papers and boards is pulping. Several processes are commonly used to convert logs to wood pulp; and these are:
 - 1) Mechanical process: Here ground pulp is produced by mechanical grinding of wood and this type of pulp produced contains all the components of the wood (cellulose, lignin, carbohydrates, resins and gums). Paper made from this type of pulp is relatively weak and dull compared to the alternative chemical process.

In the mechanical process, logs of wood are first tumbled in drums to remove the bark. The logs are then sent to grinders where they are broken down into pulp by pressing them between huge revolving slabs. The pulp is then filtered to remove foreign objects.

- 2) The Chemical process: Chemical pulp is produced by digesting wood chips in an alkaline (sulphate pulp) or acid (sulphite pulp) solution, followed by washing. This pulp is a purer form of cellulose as the other components of the wood are dissolved out during the digestion and are removed during washing.

This process takes place in huge vats called digesters. The chips are fed into the digester and then boiled at high pressure in a solution of sodium hydroxide and sodium sulfide. The chips dissolve into pulp in the solution and from hence are taken to filters where the fibers are separated from the solution. At this stage, bleach may be added or colourings and from here is sent to paper forming machine.

However, some mechanical pulp may be added to chemical pulp in paper manufacturer but such papers are not usually used in direct contact with food.

- b) Beating: This is the next step after pulping. The pulp in dilute suspension of water is subjected to controlled mechanical treatment in order to split the fibers longitudinally to produce a mass of thin fibrils. This enables them to hold together when the paper is manufactured thus increasing the strength of the paper. The structure and density of the finished paper is mainly determined by the extent of this mechanical treatment.

The beating operation is carried out in a large tub where the pulp is subjected to the effect of machine beaters which pound and squeeze the pulp at the same time. It is at this point that various filler materials can be added such as chalks, clays, or chemicals such as titanium oxide. These additives influence the opacity and other qualities of the final product. Sizing are also added at this point. Sizing affects the way the paper will react with ink without sizing at all, a paper will be too absorbent for most uses except as a desk blotter. A sizing such as starch makes the paper resistant to water-based ink (inks actually rest on top of a sheet of paper, rather than sinking in).

- c) Pulp to paper: There are two types of equipment used to produce paper from pulp.
 - 1) Fourdrinier machine: Here a dilute suspension of the pulp is deposited onto a fine woven, moving and vibrating mesh belt. By a sequence of draining vacuum filtration, pressing and drying, the water content of the flattened pulp is reduced to 4 – 8% and the network of fibres on the belt is formed into paper.
 - 2) Cylinder machine: This is mainly used for manufacture of boards where combination of different pulps is used. In this machine, six or more wire mesh cylinders which rotate partly immersed in a suspension of cellulose fiber, help to pick up fibers of cellulose and deposit them in layers into a

moving felt blanket where they are drained, vacuum filtered, pressed into a sheet and dried to moisture content of 4 – 5%.

- d) Finishing: The dried paper can further be processed depending on its ultimate use. Paper is fed to large reels where it is smoothed and compacted further by passing through metal rollers called calendars. It is during finishing operation that features like softness, dullness, hardness, shiny look can be imparted on the paper.

Types of paper used in food packaging

- 1) Kraft paper: This is made from sulphate pulp. It is available unbleached (brown) or bleached. It is a strong multipurpose paper used for wrapping individual items or parceling a number of item together. It may also be fabricated into bags and multiwall sacks.
- 2) Sulphite paper which is made from pulp produced by acid digestion. It is again a general purpose paper, not as strong as kraft paper. It is used in the form of sachets and bags e.g. sacks for flour sugar and fruits.
- 3) Greaseproof paper: Made from sulphite pulp that is given severe mechanical treatment at the beating stage. It is a close-textured paper that is impermeable to oil and grease normally used in cooking and packaging of baked products.
- 4) Vegetable parchment paper: This is a unique paper that is totally natural with unique grease and heat resistance as well as permeability properties. It is produced by passing paper made from chemical pulp through a bath of sulphuric acid, after which it is washed, neutralized and dried. The acid dissolves the surface layers of the paper, thus decreasing its porosity. It is used for packaging of fatty foods.
- 5) Tissue paper which is light and has an open structure. It is used to protect the surface of fruits and provide some cushioning.
- 6) Wet-strength papers which have chemicals added crosslinked with the fibers of the pulp. They retain more of their strength when wet compared to untreated one. They are not used in direct contact with food but mainly used for outside packaging of foods.
- 7) Wax-coated paper: Are heat-sealable and offers moderate resistance to water and water vapour transfer. However, the heat seals are relatively weak and the wax coatings may be damaged by abrasion.
- 8) Other coatings may be applied to papers to improve their functionality. These include many of the polymer materials which are applied to increase the strength of the paper, make it heat-sealable and or improve its barrier properties.

Paperboards

These are made from the same raw materials as papers. They are made on the cylinder machine and consist of two or more layers of different quality of pulp with total thickness ranging from 300 - 1100µm. the types of paperboard used in food packaging including

- 1) Chipboard: Made from a mixture of repulped waste with chemical and mechanical pulp. It is dull grey in colour and relatively weak. It is usually available lined on one side with unbleached, semi or fully bleached chemical pulp. They are seldomly used in direct contact with foods but are used as outer carton when the food is already contained in a film pouch or bag.
- 2) Duplex board: Made from a mixture of chemical and mechanical pulp, usually lined on both sides with chemical pulp. It is used for some frozen foods, biscuits and similar products.
- 3) Solid white board: The layers or plies are made from fully, bleached chemical pulp. It is used for some frozen foods, food liquids and other products requiring special protection.
- 4) Paperboards are available which are coated with wax or polymer such as polyethylene, polyvinylidene chloride and polyamides. They are mainly used for packaging wet or fatty foods.

Characteristics of paper packaging

- 1) Has appropriate strength, impact resistance and wear resistance
- 2) Good sealing and easy to clean property
- 3) Gives excellent shape and fold, easy to use in various processing methods e.g. mechanized and automated systems
- 4) Have the best printable easy introduction and landscaping of products
- 5) Lower prices, and light weight thus can reduce packaging costs and transportation
- 6) Easy to handle after use, reuse and recycling of used ones thus minimizing environmental pollution and conserving resources.

Package affects the quality of foods by controlling the degree to which factors connected with processing, storage, and handling can act on components of foods. These factors include light, oxygen concentration, moisture concentration, heat transfer, contamination,

and attack by biological agents and the ability of a package to give maximum protection to these depends on good choice selection of packaging material.

Important considerations to make when selecting a Packaging Material for a food product

Mechanical strength:

Both fresh and processed foods are susceptible to mechanical damage such as cracking of egg shell, bruising of fruits and breaking or crushing of biscuits. These damages may result from sudden impacts or shocks during handling and transportation, vibration during transportation and compression during stacking especially in warehouses. Appropriate packaging can reduce the incidence and extent of mechanical injury. Selection of strong rigid packing material such as glass, metal, wood and fiber board can reduce damage due to compression. Inclusion of cushioning material (tissues, papers, foams, plastics) as a component of a package can help protect against shocks and vibrations. Restricting movement of the product within the package can also help protect against shocks and vibrations. Restriction of movement can be done by skin tight wrapping, shrink wrapping or use of shaped containers such as egg containers.

Permeability characteristics:

The degree of permeability of a package to water vapor, gases and volatile odor compounds are important factors for consideration. Foods with high relative humidity will tend to lose moisture to the environment resulting in loss of weight and deterioration in appearance and texture. On the contrary, foods with low relative humidity will also tend to absorb moisture particularly in high humidity atmosphere leading to loss of quality. Examples are absorption of moisture by biscuits and food powders such as powdered milk, custards etc. This can lead to loss of crispness, encourage microbial action and chemical activity.

Maintaining a partial vacuum in the package (vacuum packaging) or displacing air with N_2 or CO_2 (gas packaging) may extend the shelf life of many foods by creating an atmosphere inside the package which has a low O_2 content.

Oil elusion property:

The ability of a package to prevent exit of grease or oil outside the wall of the package thereby spoiling the appearance of the pack and possibly spoiling the printings and decorations on the pack is very important. This needs to be considered especially for fatty foods.

Heat conductivity property :

A good package must be able to withstand changes in temperature which it is likely to encounter without any loss of performance or appearance. This is of particular importance when foods are to be heated or cooled in their packages.

Light transmission property:

Exposure of food to light can lead to destruction of many food components as vitamins, fading of food colors example the pink pigment (astaxanthin) and development of off

taste and flavor due to rancidity of fats. Ability of a package to prevent transmission of light through it is of great importance especially when packaging light sensitive foods. To prevent such changes due to light, packaging material which is opaque can be used or where the appearance of the food is desired, the packaging material may be colored to exclude short wavelengths of radiation. Example is amber glass commonly used for beer packaging.

Chemical and Health implication:

Compatibility of the packaging material with the food to be packaged in it is of great importance. The choice of the packaging material is such that will not allow any health issue to arise as a result of contact of the food with the package nor will permit any adverse change in the quality of the food or the integrity of the package during storage.

Microbial and rodents considerations:

One of the functions of a package is to prevent the packaged food from post process contamination as well as access to biological factors like rodents. Thus in the choice of packaging material for foods, it is important that the packaging material should be able to give an effectively sealed container that will not permit microbes and rodent accessing the packaged food. The material should also be such that cannot be eaten up by rodents.

Properties of materials that determine the degree of protection against environmental factors

1) Light-Protection characteristics of the package

The amount of light reflected, absorbed and transmitted by a package goes a long way to determine the amount of protection it can offer to the packaged food.

The fraction of incident light transmitted by any given packaging material can be considered to follow Beer-Lamberts law

$$I_x = I_0 e^{-ux}$$

Where I_x = transmitted light

I_0 = Incident light

e = Exponential

u = Absorption coefficient of the material

x = Thickness of the material

The absorption coefficient of the material depends on the nature of the material.

However the total amount of light absorbed by a food in a package is given by the following formula.

$$I_{abs} = I_o Trp \frac{1 - Rf}{(1 - Rf)Rp}$$

Where I_{abs} is the intensity of light absorbed by the food

I_o is the intensity of incident light

Trp is the fractional transmission by the packaging material

Rp is the fraction reflected by the packaging material

Rf is the fraction reflected by the food

The absorbance for both packaging material and the packaged food vary with the nature of the material or food as well as the wavelength of the radiation involved. The light barrier properties of packaging materials can be improved by special treatments like

Glass is modified by inclusion of color-producing agents or by application of coatings.

Plastics are modified by incorporation of dyes or by application of coatings

2) Permeability of the package:

The protection of foods from gas and vapor exchange with the environment depends on the integrity of the package including the seals and closures and on the permeability of the packaging material itself.

In contrast to packaging materials made from glass or metal which offer excellent barriers to various factors that induce deterioration of packaged food, packages made from polymers are permeable to varying degrees to small molecules such as gases, water vapor, organic vapors and other low molecular weight compounds. The degree of protection or barrier which they provide to the transfer of low mw molecules ranges from low to high. Knowledge of solution and transport behavior of low mw compounds in polymeric materials has become important because of their widespread use in food packaging.

There are 2 processes by which gases and vapors may pass through polymeric materials and these are:

- (1) Pore effect: This is the process in which gases and vapors flow through microscopic pores, pinholes and cracks in the materials.
- (2) A solubility-diffusion effect: In this case, the gases and vapors dissolve in the polymer at one surface, diffuse through the polymer by virtue of concentration gradient and evaporate at the other surface of the polymer. This process is sometimes described as the true permeability.

When a material is sufficiently thin, most polymers exhibit both forms of permeability. Porosity falls sharply as the thickness of the polymer is increased, reaching virtually zero

with many of the thicker types of commercially available polymer materials. True permeability however varies inversely with the thickness.

The concept of permeability is normally associated with the quantitative evaluation of the polymer barrier properties. A polymer with a good barrier has low permeability. In addition to permeability, there are two other mass transport phenomena in a package system.

- (a) Sorption (also called scalping): This involves the take-up of molecules from the food product (flavor compounds) into the package.
- (b) Migration which is the transfer of molecules originally contained in the packaging material (e.g. plasticizers, residual monomers, antioxidants) into the product and possibly to external environment.

Theory of permeability

Under a steady-state condition, a gas or vapor will diffuse through a polymer at a constant rate if a constant pressure difference is maintained across the polymer. The diffusion flux (J) of a permeant in a polymer can be defined as the amount of the permeant or substance per unit area per unit time.

$$J = \frac{Q}{At}$$

$$\left[= \left(\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right) = \text{molm}^{-2} \cdot \text{s}^{-1} \right]$$

J is used to quantify how fast diffusion of a permeant occurs

$$J = \frac{Q}{At} \dots \dots \dots (1)$$

Where Q is the total amount of permeant that has passed through an area (A) during the time (t).

The unit of J is

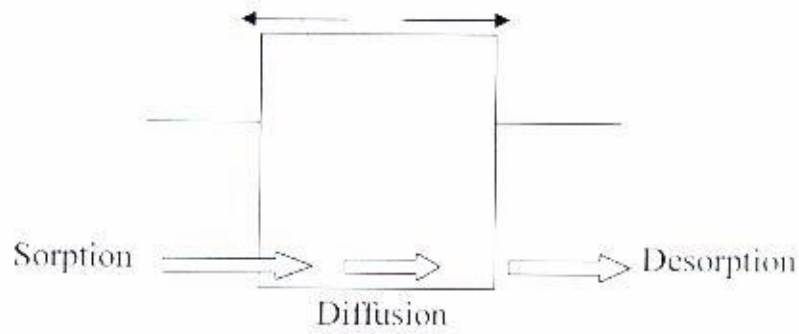
$$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} = \text{molm}^{-2} \text{s}^{-1} \text{ or } \text{molcm}^{-2} \text{sec}^{-1}$$

Using a polymeric material X mm thick of area A , exposed to a permeant at pressure P_1 on one side and at a lower pressure P_2 on the other side as shown below.

The concentration of permeant in the first layer of the polymer is C_1 and in the last layer C_2 .

P_1, P_2

C_1, C_2



The diffusion flux of the permeant can be defined as

$$J = \frac{D(c_1 - c_2)}{x} \dots \dots \dots (2)$$

Where D is the diffusion coefficient (m^2s^{-1}) of the permeant which reflects the speed at which the permeant diffuses through the polymer.

The above expression can be rewritten by substituting for J using equation (1). This becomes

$$J = \frac{Q}{At} = \frac{D(c_1 - c_2)}{x}$$

$$Q = \frac{D(c_1 - c_2)At}{x} \dots \dots \dots (3)$$

This enables us to calculate for the quantity of permeant which has diffused through a polymer of area A during a time (t).

However, when the permeant is a gas, it is more convenient to measure the vapor pressure (p) which is at equilibrium with the polymer, rather than measure the actual concentration. At sufficiently low concentrations of permeant; (c) can be expressed as

$$C = sp \dots \dots (4)$$

Where s is the solubility coefficient of the permeant in the polymer S reflects the amount of permeant in the polymer.

Coming equation (3) and (4), we have

$$Q = \frac{D(sp_1 - sp_2)At}{x}$$

$$\Rightarrow Q = \frac{DS(p_1 - p_2)At}{x} \dots \dots \dots (5)$$

The product (DS) is referred to as the permeability coefficient or permeation coefficient or permeability and can be symbolized with a capital (P).

Thus

$$Q = \frac{P(p_1 - p_2)At}{x}$$
$$P = \frac{Qx}{At(p_1 - p_2)} \dots \dots (6)$$

The term P/x is called permeance which is the total amount of protection afforded by a unit area of a barrier material.

Note: When the thickness of polymer material x is increased beyond a certain value, it becomes uneconomical to increase it further to obtain lower permeability.

Question

A polymeric material (A) with a thickness of 0.5cm and area of 32cm² was exposed to a permeant (s) with a diffusion coefficient of $0.37 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$. If the concentration of the permeant is 2.08 mol cm^{-3} and 0.85 mol cm^{-3} on either sides of the material,

- 1) Calculate the diffusion flux of the permeant
- 2) Calculate the quantity of permeant that will pass through the material in 45 sec
- 3) Calculate the permeability coefficient of the permeant given p_1 and p_2 as 85cmHg and 77cmHg.

Answers

The diffusion flux is given by the equation

$$1) \quad J = \frac{Q}{At} = \frac{D(C_1 - C_2)}{x}$$

$$J = \frac{D(C_1 - C_2)}{x}$$

Substituting for the values given, we have

$$J = \frac{0.37 \times 10^6 (2.08 - 0.85)}{0.5}$$

Answer in $910,200 \text{ mol cm}^{-2} \text{ S}^{-1}$

- 2) The quantity of permeant is given by the equation

$$Q = \frac{D(C_1 - C_2)At}{x}$$

substituting the values given, we have

$$Q = \frac{0.37 \times 10^6 (2.08 - 0.85) \times 32 \times 45}{0.5}$$

Answer in 1310688000 mol

3) The permeability coefficient is given by

$$P = \frac{Qx}{At(P_1 - P_2)}$$

substituting the values given, we have

$$P = \frac{1310688000 \times 0.5}{32 \times 45(85 - 77)}$$

Answer $56887.5 \times 10^{-11} \text{ ML (STP) cm cm}^{-2} \text{ sec}^{-1} (\text{cm Hg})^{-1}$

Note: The unit of permeability coefficient is given as

$$P = \frac{(\text{quantity of permeant under steady state})(\text{thickness})}{(\text{area})(\text{time})(\text{pressure drop across polymer})}$$

$$= \frac{10^{-11} (\text{ML at STP}) \text{ cm}}{\text{cm}^2 \text{ sec} (\text{cm Hg})}$$

$$= 10^{-11} \text{ ML (STP) cm cm}^{-2} \text{ sec}^{-1} (\text{cm Hg})^{-1}$$

PERMEABILITY PROPERTIES OF POLYMERS

The barrier properties of films depend on the specific molecular structure of the polymers involved. A structure that provides a good barrier to gases may provide a poor water vapor barrier. For e.g. a highly polar polymer that contains hydroxyl groups are excellent gas barriers but poor water vapor barriers. Their effectiveness as gas barriers is reduced when the polymer is plasticized by water. In contrast, nonpolar hydrocarbon polymers such as polyethylene have excellent water vapor barrier properties but poor gas barrier properties, the later property improving as the density of the polyethylene increases.

Diffusion of a dissolved permeant in a polymer is viewed as a series of activated jumps from one defined cavity within the polymer matrix to another. Any agent that increases

the number or size of cavities in a polymer or readers chain segments more mobile can increase the rate of diffusion.

To be a good-all round barrier material, the polymer must posses

- (1) Some degree of polarity such as is found in nitrite, chloride, fluoride etc groups
- (2) High chain stiffness: The higher the mobility of the chain segments of the polymer structure, the higher the rate of diffusion
- (3) Inertness to the permeant: The higher the interaction between the permeant and the polymer, the higher the rate of diffusion
- (4) The type of bending or attraction between polymer chains: Cross-linking of polymer chains restricts their mobility and this decreases their permeability
- (5) Close chain: Chain packing ability brought about by molecular symmetry or order, crystallinity or orientation. Linear polymers with simple molecular structure lead to good chain packing and lower permeant permeability than polymers whose structure contain bulky side groups.

Factors affecting S and D coefficients

- 1) Pressure: Increase in pressure results to increase in permeability and this only applies in situations where there is interaction between the permeant and the polymer. But a situation where there is no interaction; increase in pressure does not bring about increase in permeability hence the permeant cannot solubilize and this cannot diffuse.
- 2) Temperature: This depends more on heat of solution of the permeant (ΔH_s) where ΔH_s is positive, solubility coe increase but where ΔH_s is negative as in the case of condensation of vapour, solubility coe decreases with increase in temperature.

Because of the effect of temperature on S and D, permeability coefficient of a polymer material varies at different temperature for a particular gas. Thus the permeability coe of a polymer can be determined at a particular temperature using the equation below:

$$P = P_0 \exp(-E_p/RT)$$

Where E_p is apparent activation energy for permeation

R is the universal gas constant which is $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

T is the absolute temperature in Kelvin

P_0 is permeability of the material at absolute zero

In general, the solubility coe increases with increasing temperature for gases and decreases for vapors and the diffusion coefficient increases with temperature for both gases and vapors. For this reason, permeability coe of different polymers determined at one temperature may not be in the same relative order at other temperatures.

Calculation

- a) The permeability coe of a PET plastic bottle to CO_2 at 25°C is given as 1.6×10^{-11} [ML(STP) $\text{cm cm}^{-2} \text{sec}^{-1} (\text{cmHg})^{-1}$]. Calculate the value of B at 45°C given that $E_p = 32 \text{kJ mol}^{-1}$.
- b) Calculate the quantity of CO_2 that permeated the bottle at 45°C for 5secs given the thickness, area and pressure gradient across the bottle to e 0.07cm, 32cm^2 and 0.78cmHg^{-1} respectively.

• Solution

$$P_{25} = P_o \exp(-E_p/RT_{25}) \dots (1)$$

$$P_{45} = P_o \exp(-E_p/RT_{45}) \dots (2)$$

Using equation (1) and substituting for known values, we have

$$1.6 \times 10^{-11} = P_o \exp\left(-\frac{32,000}{8.314 \times (273 + 25)}\right)$$

$$\Rightarrow 1.6 \times 10^{-11} = P_o \exp\left(-\frac{32,000}{8.314 \times 298}\right)$$

$$P_o = \frac{1.6 \times 10^{-11}}{\exp\left(-\frac{32,000}{8.314 \times 298}\right)}$$

$$P_o = 1.6 \times 10^{-11} \exp\{32,000/(8.314 \times 298)\}$$

$$P_o = 6.507459 \times 10^{-6}$$

Substituting the value of P_o in equation (2) to get the permeability coe at 45°C we have

$$P_{45} = 6.507459 \times 10^{-6} \exp\left(-\frac{32,000}{8.314 \times 318}\right)$$

$$P_{45} = 3.56 \times 10^{-11} \{ \text{mL (STP) cm cm}^{-2} \text{Sec}^{-1} (\text{cmHg}^{-1}) \}$$

$$\text{Answer } 3.56 \times 10^{-11} [\text{ML(STP) cm cm}^{-2} \text{sec}^{-1} (\text{cmHg}^{-1})]$$

2) To calculate the quantity of CO₂ that permeated within 5secs at 45°C, we have

$$P = \frac{Qx}{At(P_1 - P_2)}$$

$$Q = \frac{P \cdot At(P_1 - P_2)}{x}$$

Substituting the known values in the equation we have

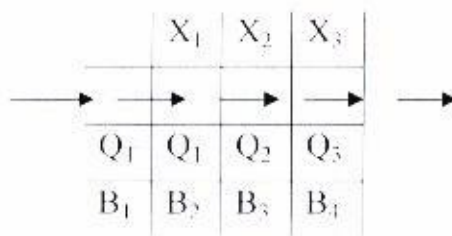
$$Q = \frac{(3.56 \times 10^{-11}) \times 32 \times 5 (0.78)}{0.07}$$

Answer 6.347×10^{-8} mol

PERMEABILITY OF MULTILAYER MATERIALS

Many foods require more protection than a single material can provide to give the product its intended shelf life. Where increased barrier to gases or moisture vapor is necessary, it is more economical to incorporate a thin layer or have a multilayer barrier material than to simply increase the thickness of the monolayer.

Multilayer materials can be considered as a number of membranes in series. Example in a 3 layer material shown below



At a steady-state flux, the rate of permeation through each layer must be constant, thus $Q_1 = Q_2 = Q_3$ and the total thickness of the material is

$$x_T = x_1 + x_2 + x_3$$

And total area of the material is

$$A_T = A_1 = A_2 = A_3$$

Then the permeability coe for multilayer material is given as

$$\frac{x_T}{P_T} = \frac{x_1}{P_1} + \frac{x_2}{P_2} + \frac{x_3}{P_3}$$

$$P_T = \frac{x_T}{\left(\frac{x_1}{P_1}\right) + \left(\frac{x_2}{P_2}\right) + \left(\frac{x_3}{P_3}\right)}$$

Where x_1 , x_2 and x_3 are the thickness of the different members that made up the multilayer.

P_1 , P_2 and P_3 are their permeability coefficients

Example

Calculate the total O_2 permeability at 30°C of a multilayer film with the following structure

	Polymer	P coe	Thickness (μm)
Layer 1	LDPE	55	50
Layer 2	Nylon 6	0.18	20
Layer 3	LDPE	55	50

Solution

Permeability coefficient of a multilayer material –

$$\frac{x_T}{P_T} = \frac{x_1}{P_1} + \frac{x_2}{P_2} + \frac{x_3}{P_3}$$

Converting the (μm) thickness to cm

$$1\mu\text{m} = 1 \times 10^{-6}\text{m}$$

$$50\mu\text{m} = 50 \times 10^{-6}\text{m} = 5 \times 10^{-5}\text{m}$$

$$1\text{m} = 100\text{cm}$$

$$\therefore 5 \times 10^{-5}\text{m} = 5 \times 10^{-5} \times 100$$

$$= 5 \times 10^{-3}\text{cm}$$

Thus 20 μm

Will give $2 \times 10^{-3}\text{cm}$

Substituting the given values in the above equation, we have

$$\begin{aligned} \frac{(5 \times 10^{-3}) + (2 \times 10^{-3}) + (5 \times 10^{-3})}{P} &= \frac{x_1}{P_1} + \frac{x_2}{P_2} + \frac{x_3}{P_3} \\ &= \frac{0.005 + 0.002 + 0.005}{P} = \frac{0.005}{55} + \frac{0.002}{0.18} + \frac{0.005}{55} \\ &= \frac{0.012}{P} = 9.091 \times 10^{-5} + 1.111 \times 10^{-2} + 9.091 \times 10^{-5} \end{aligned}$$

Thus 0.00009091

+ 0.00009091

0.01111

0.01129182

$$= \frac{0.012}{P} = 0.01129182$$

$$P = \frac{0.012}{0.01129182} = 1.0627162$$

$$P = 1.06 \times 10^{-11} [ML(STP)cmcm^{-2}sec^{-1}(cmHg)^{-1}]$$

In this example, the nylon barrier is providing virtually all of the resistance to permeability.

ASSUMPTION MADE FOR THE TREATMENT OF PERMEATION THROUGH POLYMER MATERIAL

- 1) That diffusion is at steady state or constant rate
- 2) The concentration-distance relationship through the polymer is linear
- 3) That diffusion takes place in one direction only (no net diffusion along or across it)
- 4) That both D and S are independent of concentration. This is because it is describing a permeability situation where both polymer/permeant and permeant/permeant interactions are weak relative to polymer/polymer interactions.

TRANSMISSION RATE

The permeation of organic compounds (such as flavours, aromas, odors and solvents) and water vapor through polymer film is much more complicated than that of gases. This is because their solubility coefficient and diffusion coefficient are dependent on pressure and concentration respectively. Meaning that, the higher the pressure or concentration, the higher the solubility and diffusion coefficients and the higher the permeability. Because of this, the earlier treatment of steady-state diffusion in which D and S are assumed to be independent of concentration does not apply for these permeants and their diffusion is defined as transmission rate (TR) where

$$TR = \frac{Q}{At}$$

Where Q is the amount of permeant passing through the polymer, A is the area and t is the time. Permeabilities of polymers to water and organic compounds are often presented in this way and in the case of water, the term water vapor transmission rate (WVTR) is in common usage.

Because the transmission rate (TR) includes neither pressure of the permeant nor thickness of the polymer in its dimensions, it is necessary to indicate either the pressure or the concentration of the permeant and the thickness of the polymer, under the conditions of measurement.

The unit of transmission rate is defined as ($\text{g}/\text{m}^2\cdot 24\text{h}$) while that of permeability of organic compounds and water vapor is the product of the permeance and the thickness of the test piece, assuming that the permeance is inversely proportional to thickness for homogeneous materials.

Thus permeability is

$$\text{Permeance} \times \text{thickness of test piece}$$

Where permeance is the rate of ratio of the water vapor transmission rate to the difference in vapor pressure between the surfaces of the test piece measured in (mm) mercury.

Hence permeance is

$$\frac{Q}{At} \div \Delta H_g = \frac{Q}{At(\Delta H_g)}$$

And permeability is

$$\frac{Q}{At(\Delta H_g)} \times x = \frac{Qx}{At(\Delta H_g)}$$

The unit of permeance is

($\text{g}/\text{m}^2\text{24h mmHg}$) and that of permeability is given as ($\text{cm}^3/\text{m}^2\text{24h mmHg}$) for organic vapors and water vapor.

MEASUREMENT OF PERMEABILITY

A) Gas Permeability Measurement

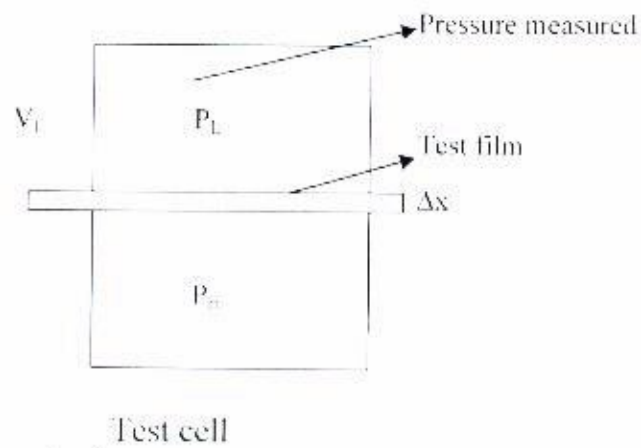
This is based on Dalton's law which says that the total pressure exerted by the gases present in a constant volume is the sum of the partial pressures of each of the gases. The partial pressure of any one of the constituent gases is the pressure that would result if that particular gas occupied the same volume by itself. The rate of permeation of a specific gas through a polymeric material is a function of the partial pressure difference of that gas across the material and not of the total pressure difference between the two sides.

Four methods for measuring gas permeability are

(1) Pressure increase method

This is the ASTM (American Std for Testing Materials) manometric method for measuring gas transmission rates and permeability of flat films. In this method, the test gas normally at 1atm is introduced on one side of the flat film or sheet, which is supported with a filter paper and sealed with an O-ring. The pressure in the receiving chamber is measured with an open-ended mercury manometer. Provided that the pressure

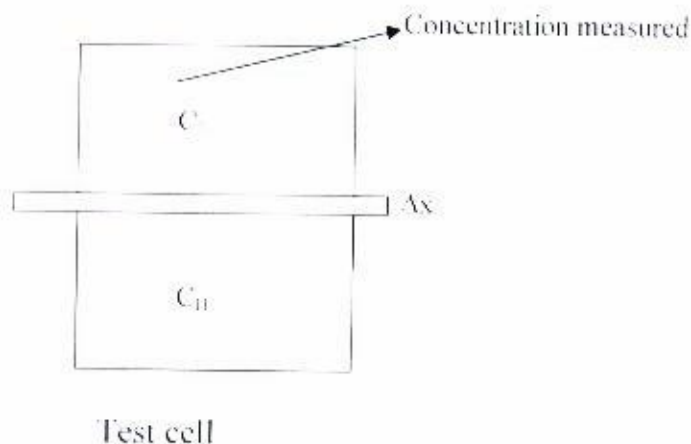
on the high-pressure side remains much larger than that on the low-pressure side, the pressure difference remains essentially constant.



Pressure-increased method

(2) Concentration increased method

In this method, the total pressure on both sides of the test material is approx equal and a partial pressure difference across the film with respect to the test gas is created without a difference in total pressure. A partial pressure difference is maintained by sweeping one side continuously with the test gas while maintaining an inert gas on the other side into which the test gas diffuses. The concentration of the test gas is then measured with time. In this method, permeability of both films and other containers such as bottles, pouches, tubes etc can be determined.



Concentration-increased method

(3) Volume-increased method

This is volumetric method in the ASTM Std. In the volumetric method, the change in volume at constant pressure due to the permeation of gas through the film is measured. Variable volume permeation cells are used for rapid measurement of relatively high steady-state permeation rates of different films.

(4) Detector film method

This is a new method of measuring permeability of films in which a little equipment is used. In this method, a plastic detector film impregnated with a reagent that is sensitive to the gas being measured is sealed between two pieces of test film in a cell, so that the permeation rate of the penetrant gas or vapor is measured.

The film has an absorption spectrum that changes as the gas or vapor is absorbed and this suitable for spectrophotometric monitoring.

(B) WATER VAPOR PERMEABILITY

The standard method to determine water vapor transmission rates is to place a quantity of desiccant in an aluminum dish which is covered with a sheet of the test material and sealed in position with wax. The dish is then placed in a closely controlled atmosphere (typically either $25 \pm 0.5^{\circ}\text{C}$ and $75 \pm 2\%$ RH for temperate conditions or $38 \pm 0.5^{\circ}\text{C}$ and $90 \pm 2\%$ RH for tropical conditions and the increase in weight noted as a function of time.

This is expressed as

$$\text{WVTR} = Q/AT$$

However, a detector film for measuring transmission rates of water vapor has also been developed and in use.

(C) PERMEABILITY OF ORGANIC COMPOUNDS

The permeability coefficient of organic compounds is highly dependent on concentration. This is because the organic compounds interact with the molecules of the polymer film causing them to swell which increases the mobility of the molecules thus increasing permeation rate. Because of this, measurement of the transport rate of organic compounds across plastics is more complicated than those of either water vapour or noncondensable gases and elaborate equipment and sensitive analytical devices are required to obtain a reliable result.

HEALTH IMPLICATIONS OF FOOD PACKAGING

The principal sources of food contamination are often enlisted as micro-organism, agrochemicals environmental chemicals, hormones used for animal production and food additives. However, recent findings have shown that the amount of material migrating from food packaging into food may well be 100 times higher than that from pesticides or environmental pollutants.

In food packaging, migration is used to describe the transfer of substances from package to the food. Substances that are transferred to the food as a result of contact or interaction between the food and the packaging material are often referred to as migrants and those have been associated with a lot of health issues. The rate of migration of substances into food is influenced by such factors as proximity of contact between the food and

packaging material involved, the environmental factors such as temperature, relative humidity, light etc.

Below are some migrants, their sources and their health implication

1 MIGRANTS FROM PLASTIC PACKAGES

- (a) Unreacted vinyl chloride monomer: Vinyl chloride is the basic material used in PVC production and it has been shown that the unreacted portion that escaped polymerization during production of PVC can migrate into packaged foods thus causing such problems as cardiac irritation, liver problems and cancer. PVC applications in food packaging include plastic bottles, film, etc. Typical examples are plastics used for biscuits, disposal cups (transparent ones) etc.
- (b) Styrene monomer: Styrene monomer is the basic material used for production of polystyrene. The unreacted monomers migrate into foods to cause health problems which are neurological and psychological in nature. E.g. of polystyrene food package is the foam-like take-away food packs.
- (c) Acrylonitrile (AN) monomer: Acrylonitrile is a component of several polymers used as food packaging materials. Example is Acrylonitrile-butadiene-styrene (ABS) resins used in many food contact applications where the levels of the three monomers in the polymers are varied to obtain different properties described in the polymer material. Acrylonitrile when migrated into food can lead to disorder of the nervous system, damage of red blood cells/liver and can cause mild symptoms like headache and nausea.
- (d) Plasticizers: These are substances incorporated into plastic materials in order to increase its flexibility and processability. Examples of these plasticizers are
 - (1) phthalate which has been shown to reduce the quantity and quality of male sperm, cause increase in testicular cancer and also marked as one of the endocrine disruptors (chemicals that enter the body from the external environment to mimic or interfere with the human endocrine system).

The majority of PVC used in food packaging does not contain phthalate plasticizers but minor uses of phthalates in food packaging including use as plasticizers in cap lines made from PVC

Phthalates are also used as plasticizers in printing inks where they assist adhesion of the ink to the packaging material and improve the ink's flexibility. Although, the inks are generally applied on the outer surface of the packaging materials and therefore are not in direct contact with the food, it has been shown that they can migrate through the plastic layer to the food.

- (2) Acetyltributyl citrate: This is also a plasticizer used in plastic films. (ATBC) migration into a variety of foods when plasticized films are used for normal domestic applications including cooking and reheating of meals in microwave oven has been proved. Ill health associated to this compound includes irritation and swollenness of skin as well as retardation of IQ.
- (3) Epoxidized soy bean oil: Epoxidized seed and vegetable oil such as epoxidized soy bean oil are widely used as multifunctional additives exhibiting plasticizing, lubricating and heat stabilizing properties. Epoxidized soy bean oil is contained in PVC gaskets used as liners for glass caps. As of present does not have any potent health effects.
- (c) Antioxidants are used in polymer materials to prevent degradation of the polymer as a result of its reaction with atmospheric O_2 or when used in contact with hot foods. They are also used to prevent embrittlement during storage. Examples of antioxidants in use as BHT and BHA (Butylated hydroxyl anisol). These are associated to cancer, asthma and behavioral issues especially in children.
- (f) Odors and Taints: Taints are unpleasant odors or flavours imparted to food through external sources while off-flavors (odors) are unpleasant odors or flavours imparted to food through internal deteriorative change occurring in the food.

Because of the complex structure and chemical composition of package systems, a variety of chemical reactions can occur during package manufacture and use. These reactions occur between some packaging components with other components acting as catalyst, resulting in the formation of compounds with low odor thresholds. These compounds can then migrate through the material during storage and slowly diffuse into the produce or package headspace. This may not have direct health implication but can lead to low acceptability of the packaged food.

Some of the odor compounds in plastics are toluene, styrene monomer, polyolefins, acetaldehyde, allyl alcohol and acrolein.

II MIGRATIONS FROM METAL PACKAGING

When tinfoil was first used to make containers for food over 150 years ago, many cases of food poisoning, apparently due to ingestion of excessive amounts of metal, occurred. Then it was recommended that tinfoil should be forbidden for the making of vessels in which articles of food are to be preserved in. However, the quality of tinfoil has greatly improved since those days, and foods which are likely to attack tin are packaged in tinfoil containers with an appropriate enamel or lacquer coating. However, these enamel coatings are not as safe as one may think because of the following.

(a) Bisphenol A: This is a known environmental estrogen that is used as the monomer to manufacture polycarbonate resins used as liners for food cans. This compound has been shown to interfere with sex hormones in both man and woman.

(b) Lead: Lead is a natural contaminant of tin as the elements co-exist in the ore. Because of this there is a level of lead in tin plate. Other source of lead in metal can is from paints (lead-based paints) and soldering areas of three-piece cans which serve as point of entry to the food.

Also tin capsules used on wine bottles can also be another source of lead into food (drinks). Lead migration from glass decanters into alcoholic beverages is another source of contamination.

Lead is poisonous and can result to death depending on the level of intake or can result to damage of some vital organs

(c) Antimony: This is a potential toxic trace element detected in foods and drinks packaged in PET. This is because it is used both as an additive and as a catalyst in the manufacture of PET. This is associated to increase in blood cholesterol and decrease in blood sugar.

(d) Aluminum: Though Al is deemed to be GRAS, it is not a part of any known animal metabolic process, in contrast to a great many less common metals involved in enzymes and other metabolic processes. High level of Al has been attributed to various disorders such as microcytic anemia etc.

(e) Chromium: In the processing of tinplates, tin layer usually undergoes a chromium treatment known as passivation in order to make it more resistant to oxidation and improve enamel adhesion. However, this compound can dissolve in the packaged food leading to contamination, though as of present no ill-effect has been attributed to this compound.

(f) Epoxy Resin Coatings: These are thermosetting resins used as can enamels. These compounds contain 2 or more epoxide groups per molecule and are formed by condensation of epichlorohydrin and Bisphenol A. Thus causing ill health problem associated to Bisphenol A.

III MIGRANTS FROM PAPER PACKING

The migrants from paper include

(a) Dioxins: This is a compound formed during the bleaching process of pulp where chlorine is used. This can also migrate into packaged foods to cause contaminations which can lead to ill health.

(b) Benzophenone: This results from inks, vanishes, lacquer etc that are cured with UV light on papers. Benzophenone is used as photoinitiators for inks and

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- (c) N-nitrosomorpholine (NMOR) and morpholine (MAR) are contaminants of paper originating from the environment and from the corrosion inhibitor used in the manufacture of paper and paper board. These compounds when ingested are converted to nitrosamines which is known to be carcinogenic.

IV MIGRANTS FROM GLASS PACKAGING

Glass is highly resistant to attack by any chemical and thus results to insignificant migration of compounds to packaged foods.

However, migration into foods packaged in glass material can come from the closures where paper, polymer material and adhesives are used which serve as sources of migrants to the foods.

LOCAL PACKAGING MATERIALS

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LOCAL PACKAGING MATERIALS



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