

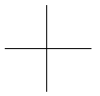
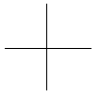
*Chapter*

**2**

# **PLASTICS AND THEIR ROLE IN FOOD PACKAGING**

*Baldev Raj*

**Food Packaging Technology Department  
Central Food Technological Research Institute  
Mysore 570 020 (INDIA)**



## PLASTICS AND THEIR ROLE IN FOOD PACKAGING

### INTRODUCTION

Food requires protection from various environmental factors from the time of its production till it is consumed. Hence, packaging is required to protect the food. The shelf life of packaged foods may range from a few days to more than a year. Thus, the properties of packaging material must have sufficient permanence to assure that shelf life is not compromised. This is not to say that the package is entirely responsible for shelf life retention. Foods deteriorate with time even with complete protection. Moreover, packages, with rare exceptions cannot improve the original quality of the food itself. Plastics are one of the greatest inventions of the millennium. Thanks to plastics, there has been enormous developments in the field of food packaging.

### PRESENT SCENARIO

Globally, plastic industries have a growth rate of 4 to 5 percent per annum, whereas, in India, it is 15%. Today, our plastic industries are able to cater to the world markets and India has acquired excellence to encash global opportunities. The consumption of basic plastics in India is about 3,915 Kilotons (KT) with polyole-

fins (polyethylene, polypropylene, etc.) at the highest level of 2,640 KT followed by PVC at 850, PS at 210, ABS at 65, PET at 75 and others at 75 KT. India is likely to become second or third largest plastic consumer from the present ninth rank in the world by the end of this decade. There are about 16 major raw material manufacturers and 23,000 small scale processing units, involving about Rs 27,000 crore of rupees turnover. Plastic materials are providing livelihoods to more than 3 million people in the country.

The overall development of plastic industry in our country is due to some useful properties of plastics. They are versatile, light weight, non-corrosive, energy efficient, durable and user friendly materials. Their aesthetic appeal, abundance, and low cost are main factors responsible for industrial growth in India. The plastic industry is larger than those of steel and aluminum because plastics enrich the quality of life by meeting the life style needs of every segment in our society. Plastics are eco-friendly and preserve the natural resources. India has become second highest economic growth region due to rapid penetration of technology. The

growth is driven by agriculture, communications, consumer goods packaging, health care, infrastructure, transportation and information technology. Plastics play an important role in fuelling the country's growth.

### **Plastics**

Plastics are the designation commonly given to both thermosetting and thermoplastic polymers, which are organic molecules consisting of many repeating units linked together to produce long chain molecules with high molecular weight (M.W.) in the range of 5,000 to 100,000. The repeating units are called "monomers". Monomers are either aliphatic, which means they do not contain long carbon chain, or aromatic, with a benzene ring as its part. In some cases, the polymer chain contains more than one kind of monomer, called copolymer and frequently the chain contains relatively short side branches. Some of the side branches may connect the long backbone chains together to make the polymer stiffer or more resistant to chemical attack. This phenomenon is known as "cross-linking".

### **Thermosets**

Thermosetting polymers harden, or "cure", when heat is applied. They cannot be remelted, and so articles made from them must be fabricated by charging the polymer ingredients to a mould, which is then heated to produce a rigid article of the required shape. Phenolics - phenol with formaldehyde, urea formaldehyde polymer were among the first plastics invented. Both these materials have good resistance to alcohols and solvents, and were frequently used for bottle and jar caps in the early days of plastics. They are used very little today in packaging. They are

basically used in closures and trays rather than primary food packaging structures. However, they are occasionally found in applications where excellent resistance to temperature extremes is important. Other thermosetting polymers include epoxies and polyurethane.

### **Thermoplastics**

Thermoplastics are the primary plastics materials now used in packaging and for a host of non-packaging applications. They dominate the universe of plastics because they can easily be formed into an almost limitless variety of shapes by heating them a number of times. The ease of fabricating plastics and the many available fabrication methods are some of the most important reasons why plastics have become such popular materials for packaging foods and beverages. Fabrication has permitted the combination of different plastics to obtain unique properties, and has also helped to produce plastics which can easily be handled on high speed packaging and printing machines. The lower energy required to fabricate plastics has combined with the reduced weight of plastics to provide considerable economic advantage for many package systems.

Thermoplastics make up the greatest share of plastic usage in food packaging because they can be rapidly formed economically into any shape needed to fulfill the package function, and are especially amenable to recycling and waste-to-energy conversion. The principal families of thermoplastics in food packaging are the polyolefins (low density or high density polyethylene, polypropylene, etc.), polystyrene, polyester, nylon, polycarbonate and vinyl polymers.

### Polyolefins

Polyolefins form an important class of thermoplastics and include polyethylene, polypropylene and some other olefinic copolymers which are among the most widely used food packaging plastics, in the form of films, mouldings, coatings, adhesives and closures. The variety of types and grades is steadily growing as manufacturers find new compositions to satisfy specific needs.



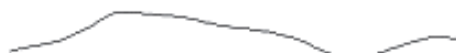
Fig. 2.1. Polyolefin based food packaging materials

(LDPE/LLDPE/HDPE/HMHDPE/PP)

### Polyethylene

Polyethylene is probably the polymer we see most in daily life. It is the most popular plastic in the world. This is the polymer that makes grocery bags, shampoo bottles, children's toys, and even bullet proof vests. For such a versatile material, it has a very simple structure, the simplest of all commercial polymers. A molecule of polyethylene is nothing more than a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atom.

polyethylene, or High Density Polyethylene (HDPE). Linear polyethylene is much stronger than branched one.



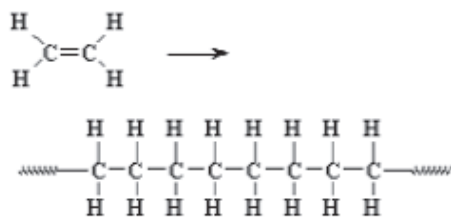
A molecule of linear polyethylene, or HDPE



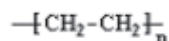
A molecule of branched polyethylene, or LDPE

Sometime some of the carbons, instead of having hydrogens attached to them, will have long chains of polyethylene attached to them. This is called branched, or low-density polyethylene, or LDPE. When there is no branching, it is called linear

It is normally produced with molecular weights in the range of 200,000 to 500,000, but it can be made even with higher M.W. Polyethylene with molecular weights of three to six million is referred to as ultra-high molecular weight polyethylene, or UHMWPE. This can be used to make strong fibers used in bullet proof vests.



or



### Low Density Polyethylene (LDPE)

This is the largest volume single polymer used in food packaging in both film and blow-molded forms. It is a polymer of ethylene, a hydrocarbon gas

available in large quantities as a by-product of petroleum refining and other process. Polyethylene was first produced by Imperial Chemical Industries (ICI) Limited in 1933, under extremely high pressure on chain reactions. It was produced on a pilot plant scale that same year with full commercial scale production commencing in 1939.

The polymerization of ethylene can occur over a wide range of temperatures and pressures but most commercial high pressure processes utilize pressures between 1,000 and 3,000 atmospheres and temperatures between 100° and 350°C; higher temperatures causing degradation of the polyethylene.

The simplest structure for polyethylene is a completely unbranched structure of  $-CH_2-$ . The vigorous nature of the high pressure process leads to a great extent of chain branching, with both short and long chains being formed. The branch chains prevent close packing of the main polymer chains and this results in the production of relatively low density polyethylenes (typically 0.91-0.94 g/cm<sup>3</sup>). Areas where the chains are parallel and closely packed are largely crystalline, while disordered areas are amorphous. The crystalline areas are known as crystallites. When the polymer melt is cooled slowly, the crystallites may form spherulites.

The crystallinity of LDPE usually varies between 50 and 70%. The softening point is affected by chain branching. Because the chains are unable to approach each other closely, the attractive forces between them are reduced and less energy (in form of heat) is necessary to cause them to move relatively to each other and thus flow. The softening point of LDPE is just below

100°C, thus precluding the use of steam to sterilize it in certain food packaging applications.

LDPE is a tough, slightly translucent material, which can be blown extruded into tubular film, or extruded through a slit die and chill-roll cast, the latter process giving a clearer film. It has good tensile strength, burst strength, impact resistance and tear strength, retaining its strength down to -60°C. While it is an excellent barrier to water and water vapour, it is not a good barrier to gasses.

LDPE has excellent chemical resistance, particularly to acids, alkalis and inorganic solutions, but is sensitive to hydrocarbons and halogenated hydrocarbons and to oils and greases. These compounds are absorbed by the LDPE, which then swells. Environmental stress cracking (ESC) is a phenomenon, which occurs when a material is stressed multi-axially while in contact with certain polar liquids or vapours, resulting in surface cracks or even complete failure of the material. Essential oils and vegetable oils are capable of causing ESC but the effect can be greatly reduced by using high molecular weight grades of LDPE. One of the great attributes of LDPE is its ability to be fusion welded to itself to give good, tough, liquid-tight seals.

LDPE is also used as a rigid packaging material. It can be easily blow moulded into bottles where its flexibility enables the contents to be squeezed out. It is also widely used in the form of snap-on caps, collapsible tubes and a variety of spouts and other dispensers. The surface of polyethylene containers can be treated with fluorine after blow molding to form a very thin polar, cross-linked surface, which

decreases the permeability of the polyethylene to nonpolar penetrants. It also eliminates the need for treating the surface by corona-arc discharge or flame techniques to improve printability properties. Polyethylene is one of the most inert polymers and causes no hazard in normal handling.

### **Linear Low Density Polyethylene (LLDPE)**

The first production of LLDPE was made in a solution process in 1960. Attempts in the 1970's to produce LDPE, either by low-pressure gas phase polymerization or by liquid phase process similar to those used for producing HDPE, led to the development of LLDPE, which has a molecular structure similar to HDPE. However, it is virtually free of long chain branches but does contain numerous short side chains. It is manufactured as a result of copolymerizing ethylene with a smaller amount of higher alkenes such as propene, 1-butene, 1-hexene or 1-octene. Such branching interferes with the ability of the polymer crystallization, and therefore results in LLDPE having a density similar to LDPE. The linearity provides strength, while the branching provides toughness. The term linear in LLDPE is used to imply the absence of long chain branches. It was after 1977 that LLDPE became available in commercial quantities.

A major feature of LLDPE is that its molecular weight distribution is narrower than that of LDPE. Generally, the advantages of LLDPE over LDPE are improved chemical resistance, improved performance at both low and high temperatures, higher surface gloss, higher strength at a given density and a greater resistance to environmental stress cracking. In film form,

LLDPE shows improved puncture resistance and tear strength. At a density of 0.92 g/cm<sup>3</sup>, the melting points of LDPE and LLDPE are 95°C and 118°C, respectively. LLDPE commonly has a density of around 0.92 g/cm<sup>3</sup>, with butene in particular, as the comonomer. The superior properties of LLDPE have led to its use in new applications for polyethylene as well as the replacement of LDPE and HDPE in some areas, specially in liquid packaging of milk, arrack, etc.

### **High Density Polyethylene (HDPE)**

Prior to 1950, the only commercial polymer of ethylene was the highly branched polymer LDPE. The technique for making a linear polymer was discovered by Nobel laureate Karl Ziegler of Germany in the early 1950's. Ziegler prepared HDPE by polymerizing ethylene at a low pressure and at ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Relatively low pressure/low temperature polymerization processes at 27-34 atmospheres and 100-175°C or 20 atmospheres and 85-100°C are used to produce HDPE.

HDPE possesses a much more linear structure than LDPE and has up to 90% crystallinity compared to LDPE which exhibits crystallinity as low as 50%. Although some branch chains are formed, these are short and few in number. HDPE film is stiffer and harder than LDPE and densities range from 0.94-0.96 g/cm<sup>3</sup>. Its softening point is about 121°C, and its low temperature resistance is almost the same as LDPE. Tensile and bursting strengths are higher but impact and tear strengths are both lower than LDPE due to the linear nature of the HDPE molecules. They tend

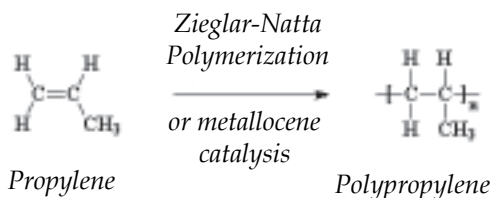
to align themselves in the direction of flow and thus the tear strength of the film is much lower in the machine direction compared to the transverse direction.

The chemical resistance of HDPE is also superior to that of LDPE and, in particular, it has better resistance to oils and greases. The film offers excellent moisture protection, a much decreased gas permeability compared with LDPE film, but is much more opaque. Heat sealing is considerably more difficult compared to LDPE film.

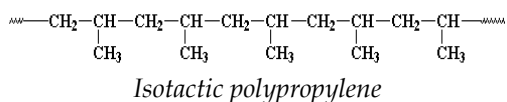
HDPE film has a white, translucent appearance and therefore tends to compete with paper. HDPE is blow molded into bottles, jars, jerricans, etc., for a variety of food packaging applications.

## Polypropylene (PP)

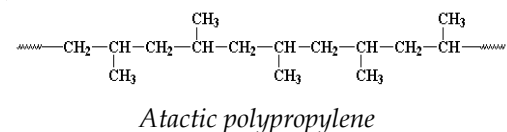
Structurally, PP is a vinyl polymer and is similar to polyethylene except that the backbone chain has a methyl group attached to it on every other carbon atom. Polypropylene can be made from the monomer propylene by Ziegler-Natta polymerization and by metallocene catalysis polymerization.



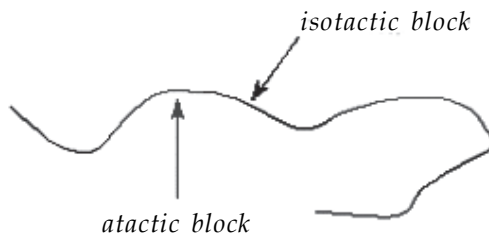
Polypropylene can be made with different tacticities. Most polypropylene we use is *isotactic*. This means that all the methyl groups are on the same side of the chain, as shown below:



But sometimes we also use *atactic* polypropylene. *Atactic* means that the methyl groups are placed randomly on both sides of the chain as shown below:



This atactic PP is soft and rubbery in nature. However, using special metallocene catalysts it is believed that we can make polymers which contain blocks of isotactic polypropylene and blocks of atactic polypropylene in the same polymer chain, as shown below.



This polymer is rubbery, and makes a good elastomer. Because the isotactic blocks form crystals by themselves and are joined to the atactic blocks, soft rubbery tethers of atactic polypropylene will tie each little hard clump of crystalline isotactic polypropylene together.

PP can be blow moulded and injection molded, the latter process being widely used to produce closures and thin walled pots and crates. The glass transition temperature of PP is placed between 10°C and -20°C with the result that the polymer becomes brittle as subzero temperatures are



approached. Copolymerization with 4-15% of ethylene improves the strength and lowers the  $T_m$  and  $T_g$  slightly; such copolymers are often preferred to the homopolymer in injection molding and bottle blowing applications, and also find use in shrink-wrapping where the lower melting point is an advantage.

PP has a lower density ( $0.90 \text{ g/cm}^3$ ) and a higher softening point ( $140^\circ\text{-}150^\circ\text{C}$ ) than the polyethylenes, low water vapor transmission, medium gas permeability, good resistance to greases and chemicals, good abrasion resistance, and high temperature stability, as well as good gloss and high clarity, the latter two factors making it ideal for reverse printing.

Non-oriented PP film is often referred to as cast PP (CPP) film because it is generally made by the chill-roll cast process, although other methods can be used. PP film is a very versatile material being used as a thermoformable sheet, in cast form for film and bags, and as thin, strong biaxially oriented film for many applications. Cast and oriented PP are sufficiently different as they do not compete for the same end use. The cost of cast PP is much lower than that of oriented PP. The cast form has polyethylene type uses while the oriented form has regenerated cellulose type uses. Cast PP use in food packaging is limited owing to its brittleness at below-freezing temperatures, and it is generally not recommended for use with heavy, sharp or dense products unless laminated to stronger, more puncture-resistant materials. The relatively high temperature resistance of PP permits its use as the sealant layer in retortable pouches where temperatures of up to  $130^\circ\text{C}$  are encountered.

Polypropylene is one of those rather versatile polymers. It serves double duty, both as a plastic and as a fiber. As a plastic it is used to make things like dishwasher-safe food containers. It can do this because it doesn't melt below  $160^\circ\text{C}$ . As a fiber, polypropylene is used to make indoor-outdoor carpeting, the kind that is used around swimming pools and miniature golf courses. It works well for outdoor carpet because it is easy to make colored polypropylene, and the polypropylene doesn't absorb water like nylon.

### **Oriented Polypropylene (OPP)**

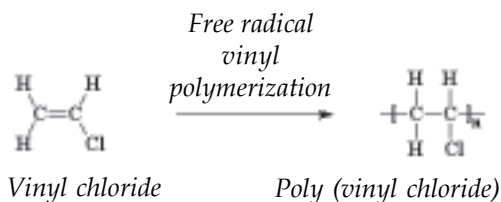
In recent years there has been a large increase in the use of oriented polypropylene (OPP) for food packaging. Wide variations are possible in the extent of orientation in two directions, leading to a wide range of properties. However, biaxially oriented (BOPP) film has a high clarity since layering of the crystalline structures reduces the variations in refractive index across the thickness of the film and this in turn reduces the amount of light scattering. The blown tubular or high expansion bubble process, or the tenter frame process can produce OPP.

BOPP film has a tensile strength in each direction roughly equal to four times that of cast PP film. Although tear initiation is difficult, tear resistance after initiation is low. Biaxial orientation also improves the moisture barrier properties of PP film and its low temperature impact strength. OPP film is not considered to be a gas barrier film but this deficiency can be overcome by coating with poly(vinylidene chloride) (PVDC) copolymer. OPP films often have a stiff feel and tend to crinkle audibly.

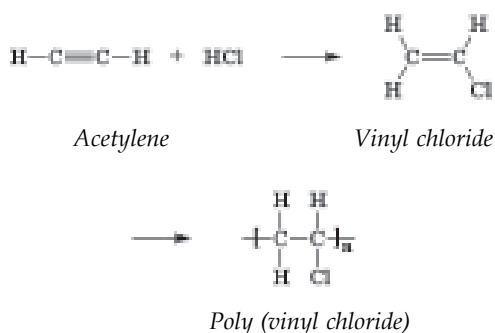
If heat sealing is required, PP is normally coated with a lower melting point polymer because shrinkage tends to occur when highly stretched film is heated. PE, PVDC copolymer and acrylic polymers are used as fusible coatings for OPP film. Though PE is cheaper, PVDC copolymer confers far better resistance to water vapor and oxygen permeability. Acrylic polymer adds no barrier properties to OPP.

### Poly (Vinyl Chloride) (PVC)

Structurally, PVC is a vinyl polymer. It is similar to polyethylene, but on every other carbon in the backbone chain, one of the hydrogen atoms is replaced with a chlorine atom. It is produced by the free radical polymerization of vinyl chloride.



PVC was one of those odd discoveries a hundred years ago, in Germany. It was prepared using acetylene and hydrochloric acid in 1912 by one German chemist, Fritz Klatte:



Poly (vinyl chloride) is the plastic known at the hardware store as PVC. This is the PVC from which pipes are made, and PVC pipe is everywhere. The "vinyl" siding used on houses is made of poly (vinyl chloride). Inside the house, PVC is used to make linoleum for the floor. In the seventies, PVC was often used to make vinyl car tops. PVC is useful because it resists two things that hate each other: fire and water. Because of its water resistance, it is used to make raincoats and shower curtains, and of course, water pipes. It has flame resistance too, because it contains chlorine. When PVC is burnt, chlorine atoms are released and chlorine atoms inhibit combustion.

Addition polymerization of VCM produces poly (vinyl chloride) (PVC). From the structure of VCM, it can be seen that addition of molecules to the growing chain can take place either head to head, head to tail or in a completely random manner. PVC polymerizing in either of the first two forms would be expected to be crystalline, while those containing the random arrangement would be amorphous. Generally, PVC polymerizes in the atactic form and thus is largely an amorphous polymer.

Vinyl polymers and copolymers make up one of the most important and diversified groups of linear polymer. This is because PVC can be compounded to produce a wide spectrum of physical properties. This is reflected in the variety of uses to which it is put - from exterior guttering and water pipes to very thin flexible surgical gloves.

It is the second most widely used synthetic polymer after polyethylene and is commonly referred to simply as "vinyl". A

range of PVC films with widely varying properties can be obtained from the basic polymer. The two main variables are changes in formulation (principally plasticizer content) and orientation. The former can give films ranging from rigid, crisp films to limp, tacky, stretchable films. The degree of orientation can also be varied from completely uniaxial to balanced biaxial.

Unplasticized PVC tends to degrade and discolour at temperatures close to those used in its processing. So suitable stabilizers have to be included in the formulation. The stabilizers used are generally the salts of tin, lead, cadmium, barium, calcium or zinc along with epoxides and organic phosphates, and they must be carefully selected for non-toxic

applications. The amount of residual VCM present in the polymer resin or formed during blow moulding must be kept within the legal limits set.

Approval by US Food and Drug Administration of certain octyltin compounds for use in stabilizing PVC during blow moulding of containers has expanded the use of this polymer for food packaging.

Extremely clear and glossy films can be produced having a high tensile strength and stiffness. The density is high at around  $1.4 \text{ g/cm}^3$ . The water vapour permeability is higher than that of the polyolefins but the gas permeability is lower. Unplasticized PVC has excellent resistance to oils, fats and greases and is also resistant to acids and alkalis.

To a large extent, the properties of plasticized PVC depend on the type of plasticizer used, as well as the quantity. For these reasons it is difficult to be very specific about the physical properties of PVC and as such a wide range of plasticization is possible.

Films with excellent gloss and transparency can be obtained provided that the correct stabilizer and plasticizer are used. Both plasticizer and unplasticizer films can be sealed by high frequency welding techniques. PVC is inert in its chemical behaviour, being self-extinguishing when exposed to a flame.

Thin plasticizer PVC film is widely used in supermarkets for the stretch wrapping of trays containing fresh red meat and produce. The relatively high water vapour transmission rate of PVC prevents condensation on the inside of the film. Orientation films are used for shrink wrapping of produce and fresh meat.



Fig. 2.2. PVC based food packaging materials (Thermoformed/Clingwrap)

Unplasticized PVC as a rigid sheet material is thermoformed to produce a wide range of inserts from chocolate boxes to biscuit trays. Unplasticized PVC bottles have better clarity, oil resistance and barrier properties than those made from polyethylene. However, certain solvents, notably ketones and chlorinated hydrocarbons soften them. PVC bottles have made extensive penetration into the market for a wide range of foods including fruit juices and edible oils. Today, PET bottles are completely replacing PVC bottles, due to their poor impact resistance and tainting problems due to stabilizers.

### **Poly (Vinylidene Chloride) (PVDC)**

Pure poly (vinylidene chloride) homopolymer yields a rather stiff film which is hardly suited for packaging purposes. However, when it is copolymerized with 5 to 50% (but typically 20%) of vinyl chloride, a soft, tough and relatively impermeable film results. The Dow Company has been marketing these copolymers since 1940 under the trade name "Saran".

The properties of PVDC copolymer film include a unique combination of low permeability to water vapor, gases and odours, as well as greases and alcohols. It has good stress-crack resistance to a wide variety of agents. It also has the ability to withstand hot filling and retorting, making it a useful component in multilayer barrier container. It is an important component of many laminates and is the best coating for regenerated cellulose. PVDC copolymers can be sealed to themselves and to other materials.

By itself, the copolymer is frequently used as a shrink film since orientation

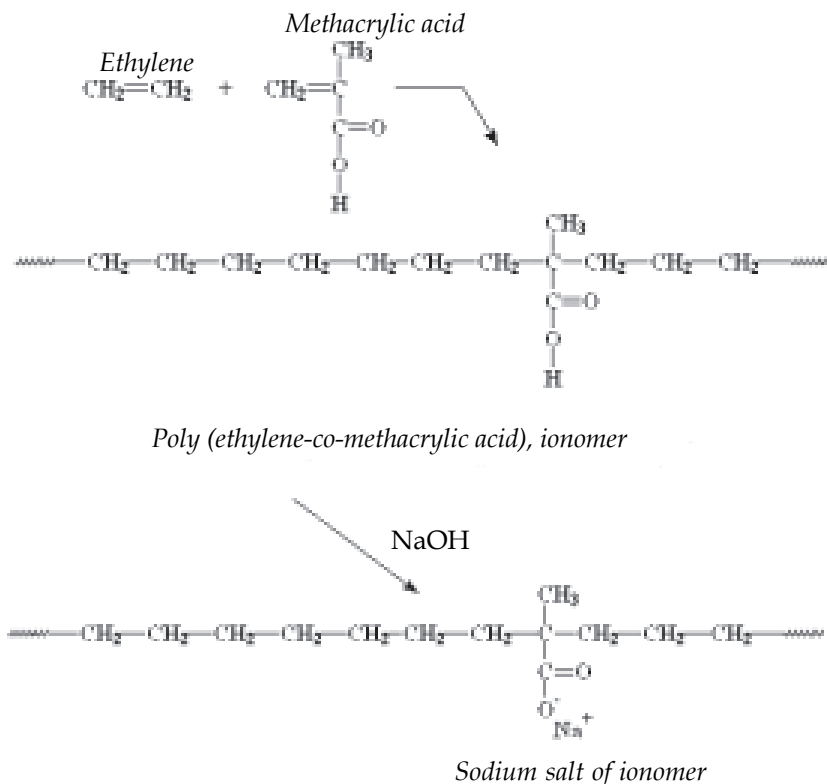
improves tensile strength, flexibility, clarity, transparency and impact strength. As well, gas and moisture permeability are lowered and tear initiation becomes difficult. The shrink film can be heat sealed using impulse sealing with teflon-coated heating bars.

### **Ionomers**

These were first discovered by Du Pont in the 1960s, and are prepared by copolymerizing ethylene with a small amount of (1-10%) unsaturated carboxylic acid such as methacrylic acid/acrylic acid using the high pressure process. These polymers are called ethylene acrylic acid copolymer (EAA)/ethylene methacrylic acid copolymer (EMA). Further, such copolymers are neutralized to varying degrees with the derivative of a metal such as sodium methoxide or magnesium; ionize cross links which confers enhanced stiffness and toughness (the puncture resistance of ionomer film is double that of LDPE film of the same gauge) on the material at ambient temperatures.

One example of an ionomer is poly (ethylene-co-methacrylic acid). This polymer is a sodium or zinc salt (which provides the ions) of copolymers derived from ethylene and methacrylic acid, commercially branded as "Surlyn".

In an ionomer, the nonpolar chains are grouped together and the polar ionic groups are attracted to each other. The ionic groups would like to go off into a little corner by themselves, but since they are attached to the polymer chain, they cannot do so. This allows thermoplastic ionomers to act in ways similar to that of crosslinked polymers or block copolymers.



In comparison with LDPE, ionomer/EAA/EMA films have excellent oil and grease resistance, excellent resistance to stress cracking, greater clarity, lower haze, greater abrasion resistance and a higher moisture vapor permeability due to lower crystallinity. Their disadvantages include their poorer slip and block characteristics. Ionomers are particularly useful in composite structures to provide an inner layer with good heat sealability. Laminated or co extruded films with nylon or polyesters are widely used for packaging meat, cheese and vegetable oils. The resulting ionic attractions strongly influence the polymer properties.

However, ionomers are not crosslinked polymers, and are in fact a type of

thermoplastic called a reversible cross-linker. When heated, the ionic groups will lose their attractions for each other and the chains will move around freely. As the temperature increases, the chains move around faster and faster and the groups cannot stay in their clusters. This allows for a polymer with the properties of an elastomer and the processability of a thermoplastic. These ionomers are sometimes known as thermoplastic elastomers.

EAA copolymer resin is normally processed at melt temperatures ranging from 190 to 218°C in blown film equipment. The resin is available for use in blown and cast film extrusion and coextrusion equipment, designed to process polyethylene

resins. They exhibit better properties in comparison with LDPE, e.g. EAA has excellent adhesion to coextruded nylon for superior structure reliability with high film strength and barrier integrity for product protection. It has very good hot tack, sealability through contamination especially edible vegetable oils, and heat seal strength for strong, reliable heat seals. EAA has wide use in meat, poultry, seafood, and cheese packaging, edible oils and other liquid product pouches.

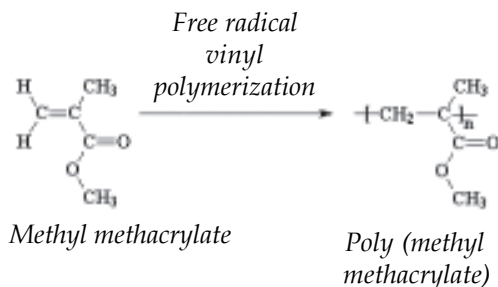
### Acrylates

Acrylates are a family of polymers, which are a type of vinyl polymer. These are of course, made from acrylate monomers. Acrylate monomers are esters, which contain vinyl groups, that is, two-carbon atoms double bonded to each other, directly attached to the carbonyl carbon.

Some acrylates have an extra methyl group attached to the alpha carbon, and these are called methacrylates. One of the most common methacrylate polymers is poly(methyl methacrylate) (PMMA).

### Methacrylate

This little methyl group would make a whole lot of difference in the behavior and properties of the polymer. Poly (methyl acrylate) is a white rubber at room



temperature, but poly (methyl methacrylate) (PMMA) is a strong, hard, and clear plastic.

PMMA is a vinyl polymer made by free radical vinyl polymerization from the monomer methyl methacrylate.

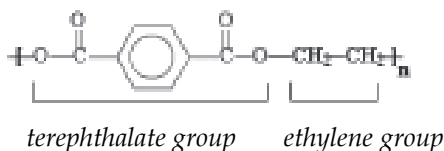
As it turns out, how soft or hard a polymer is at a given temperature is determined by what we call chain mobility that is how well the polymer chains wiggle past and around each other. If the polymer chains can slither and wiggle past and around each other easily, the whole mass of them will be able to flow more easily. So a polymer, which can move around easily, will be soft, and one which cannot, will be hard.

When it comes to making windows, PMMA has another advantage over glass. PMMA is more transparent than glass. When glass windows are made too thick, they become difficult to see through. But PMMA windows can be made as much as 13 inches (33 cm) thick, and they are still perfectly transparent. This makes PMMA a wonderful material for making large aquariums, whose windows must be thick in order to contain the high pressure of millions of gallons of water.

### Polyesters

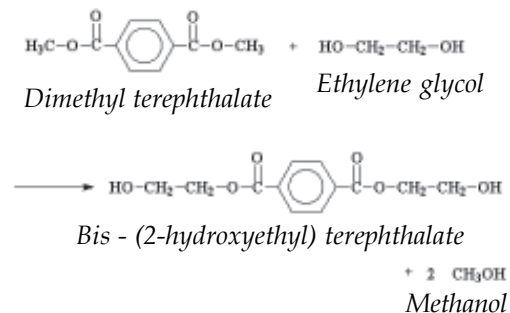
Simple polyesters are derived from condensation of polyhydric alcohol and a polyfunctional acid and are sometimes described as alkyds (from alcohol and acid). Each component needs a functionality (i.e., number of reactive groups such as -OH, -COOH, per molecule of 2 to form a linear chain, while if one (or both) monomers have a functionality of at least 3, cross-linkage can occur resulting in a much more rigid 3-D lattice structure. Poly

(ethylene terephthalate) (PET) can be produced by reacting ethylene glycol with terephthalic acid, although in practice the dimethyl ester of terephthalic acid is used to give a more controllable reaction. Methanol is generated as the product of the exchange reaction and can be recovered for further use. Polyesters have hydrocarbon backbones, which contain ester linkages, hence, the name ester. The structure in the picture is called poly (ethylene terephthalate), or PET for short, because it is made up of ethylene groups and terephthalate groups.



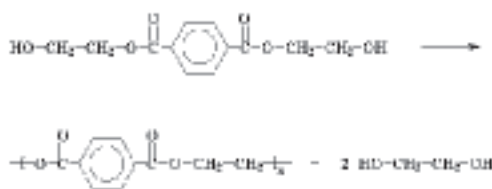
The ester groups in the polyester chain are polar, with the carbonyl oxygen atom having a somewhat negative charge and the carbonyl carbon atom having a somewhat positive charge. The positive and negative charges of different ester groups are attracted to each other. This allows the ester groups of nearby chains to line up with each other in crystal form that is why they can form strong fibers.

In big plants where they make polyester with a compound called dimethyl terephthalate, which is reacted with



ethylene glycol, the reaction is called transesterification. The result is bis-(2-hydroxyethyl) terephthalate and methanol.

The bis-(2-hydroxyethyl) terephthalate is also heated up to a temperature of 270 °C, and it reacts to give the poly(ethylene



Ethylene glycol

Poly (ethylene terephthalate)

terephthalate) and, oddly, ethylene glycol as a byproduct.

But in the laboratory, PET is made by other reactions. Terephthalic acid and ethylene glycol can polymerize to make PET when the reaction mixture is heated with an acid catalyst. The product has a carboxyl group at one end and a hydroxyl group at the other, so it can condense with another molecule of alcohol and acid. The molecules grow to a molecular weight of up to 20,000.

PET is well known as a fiber (trade names include Terylene, Crimpylen, Kodel, Dacron and Trevira) and as a film (trade names include Mylar, Scotchpak, Celenar, Esterfane, Vindenem Melinex and Hostaphane).

PET has a melting point ( $T_m$ ) of 267°C and a glass transition point ( $T_g$ ) between 67° and 80°C. PET films are most widely used in the biaxially oriented, heat stabilized form. There are virtually no applications for the material in its un-oriented form because, if crystalline, it is extremely brittle and opaque, and if

amorphous, it is clear but not tough. In a two-stage process, machine direction stretching induces 10-14% crystallinity and this is raised to 20-25% by transverse orientation. In order to stabilize the biaxial orientation, the film is annealed (or heat set) under restraint at 180°-210°C, which increases the crystallinity to around 40% without appreciably affecting the orientation, and reduces the tendency to shrink on heating. Subsequent coatings are applied to obtain special barrier properties, slip characteristics or heat sealability.

PET film's outstanding properties as a food packaging material are its great tensile strength, excellent chemical resistance, lightweight, elasticity and stability over a wide range of temperatures (-60° to 220°C). This latter property has led to the use of PET for "boil-in-bag" products, which are frozen before use (PET is usually laminated to or extrusion coated with LDPE and is typically the outside and primary support film of such laminations), and as oven bags where they are able to withstand cooking temperatures without decomposing.

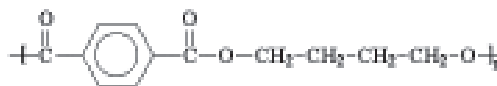
To improve the barrier properties of PET, coatings of either LDPE, PVDC copolymer or PVDCcoAN have been made. PET film extrusion-coated with LDPE is very easy to seal and very tough. It can be sealed over powders and some liquids, the integral seal will withstand sterilization by UV. Two-side PVDC copolymer coated grades provide a high barrier and a major special application is the single-slice cheese wrap.

Metallization of PET films results in a considerable improvement in barrier properties. A reduction in water vapor transmission rate by factor of 40 and oxygen permeabilities by over 300 are obtained.

A fast-growing application for PET is

"ovenable" tray for frozen food and prepared meals, where they are preferred over foil trays because of their ability to be microwaved without the necessity for an outer board carton. These trays are thermoformed from cast PET film and crystallized by heat-setting the trays which prevents deformation during cooking and serving.

A relatively new polyester resin being considered for co-extruded structures is poly-(butylene terephthalate) (PBT) where 1,4-butanediol is used instead of ethylene glycol. It offers good gas barrier properties together with good tensile strength, retaining these properties at elevated temperatures. PBT can be steam sterilized, thus making it eminently suitable for high-temperature applications such as hot-fill applications and boil-in-bag products. Although PBT does not have good heat seal characteristics, it could be co-extruded with EVA to yield a heat sealable structure. Both cast and blown co-extruded films have been made, and they can be used in the



*Poly (butylene terephthalate)*



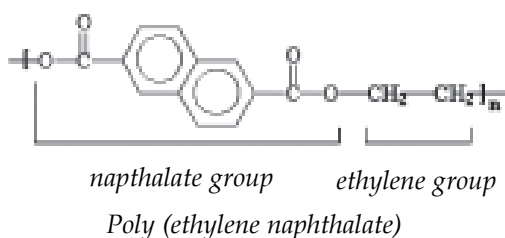
*Poly (trimethylene terephthalate)*

unoriented form since their tensile strength is better than unoriented PET.

In the late 1970's, the benefits of biaxial orientation of PET were extended from sheet film to bottle manufacture. As a result important new markets have been opened up, particularly for carbonated



beverages. The bottles are stretch-blow moulded. The stretching or biaxial orientation is necessary to get maximum tensile strength and gas barrier, which in turn enables bottle weights to be low enough to be economical. However, the use of stretch blown bottles is restricted upto 60°C temperature, beyond this temperature, the bottles start shrinking.



There is a new kind of polyester that is well suited for jelly jars and returnable bottles. It is poly(ethylene naphthalate), or PEN.

PEN has a higher glass transition temperature than PET. That is the temperature at which a polymer gets soft. The glass transition temperature of PEN is high enough so that it can withstand the heat of both sterilizing bottle washing and hot

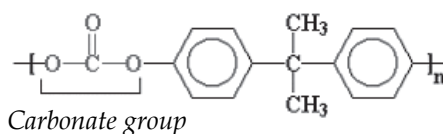


Fig. 2. 3. PET based food packaging materials (films/laminates/containers)

strawberry jelly. PEN is so good at standing the heat that it is not necessary to make the bottle entirely out of it. Just mixing some PEN with the PET gives a bottle that can take the heat a lot better than plain PET.

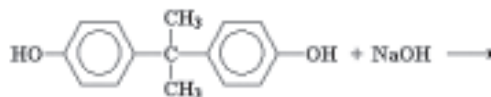
### Polycarbonates

Polycarbonates (PC) are polyesters of unstable carbonic acid and have carbonate linkages. They were originally produced by the reaction of phosgene (COCl<sub>2</sub>) with bisphenol A [2, 2' - bis (4-hydroxyphenyl) propane]. Bisphenol A is still the most commonly used phenol but diphenyl

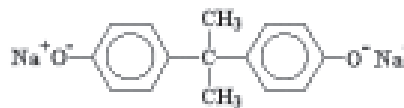


carbonate has replaced phosgene.

Polycarbonate, or specifically polycarbonate of bisphenol A, is a clear plastic used to make shatterproof windows, lightweight eyeglass lenses, etc.



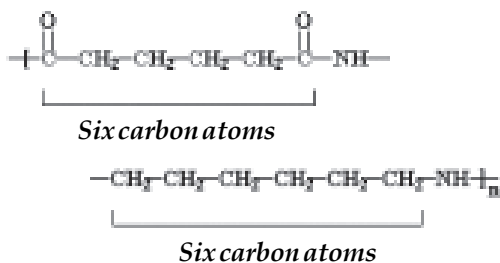
Bisphenol A



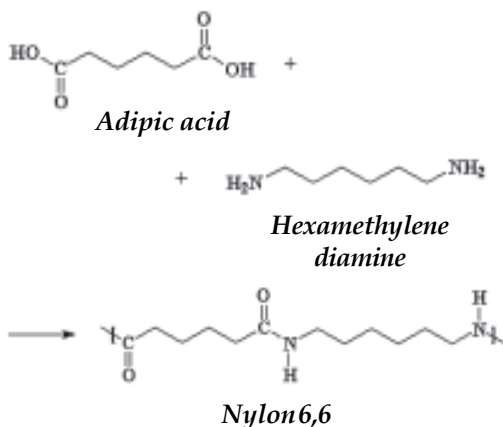
Sodium salt of bisphenol A

Polycarbonate gets its name from the carbonate groups in its backbone chain. It is called as polycarbonate of bisphenol A because it is made from bisphenol A and

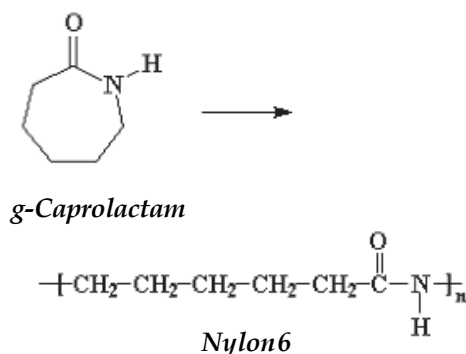




bond with each other. Because of this, and as the nylon backbone is so regular and symmetrical, nylons are often crystalline and make very good fibers. The nylon in



the figure below is called nylon 6,6, because each repeat unit of the polymer chain has two stretches of carbon atoms, each being six carbon atoms long.



Other nylons can have different numbers of carbon atoms in these stretches. It is usually made by reacting adipic acid with hexamethylene diamine:

Another kind of nylon is nylon 6. It is similar to nylon 6,6 except that it only has one kind of carbon chain, which is six atoms long.

It is made by a ring opening polymerization from the monomer caprolactam. Nylon 6 does not behave much differently from nylon 6,6. The only reason that both of them have come into existence is because DuPont patented nylon 6,6, so other companies had to invent nylon 6 in order to enter nylon business.

Thus it can be seen that two different types of nylon films are available based on their resin manufacture. One type is made by a condensation of mixtures of diamines and dibasic acids. These are identified by the number of carbon atoms in the diamine, followed by the number of carbon atoms in the diacid. The other type is formed by a condensation of single, hetero functional amino acids, known as ω-amino acids since the amino and carboxyl groups are at opposite ends of the polyamides. A single number signifying the total number of carbon atoms in the amino acid is used for its identification.

Several nylons have been produced with chains greater than six-carbon atoms, as they result in films with a lower melting point and an increased resistance to water vapour. Again, the key to successful commercialization is to find cheap sources of the monomers.

In general, nylons are highly permeable to water vapour, the absorbed water having a plasticizing effect which causes

a reduction in tensile strength and an increase in impact strength. Their permeability to oxygen and other gases is quite low when the films are dry. PVDC copolymer coated nylons offer improved oxygen and moisture vapour and UV light barrier properties. Odour retention is excellent and the films are tasteless, odourless and nontoxic.

Biaxial orientation of nylon films provides improved flex-crack resistance, mechanical and barrier properties. These films have new applications in packaging foods such as processed and natural cheese, fresh and processed meats, and frozen foods. They are used in pouches and bag-in-box structures. In some applications, nylons compete with biaxially oriented PET. Although oriented nylons offer better gas barrier, softness and puncture resistance, oriented PET offers better rigidity and moisture barrier. It is mostly used as a middle layer in coextruded films for oil packaging with a contact layer of EAA and LDPE as outer layer.

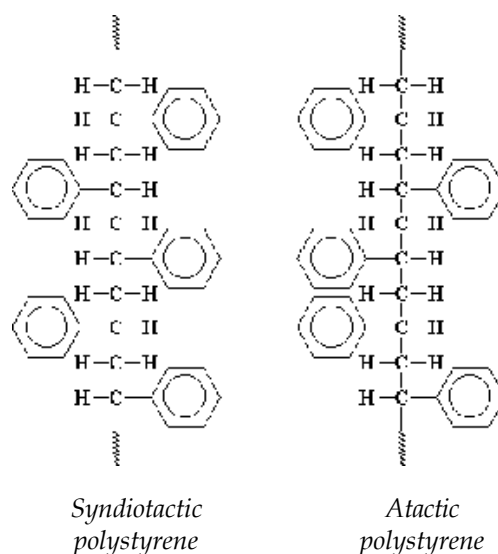
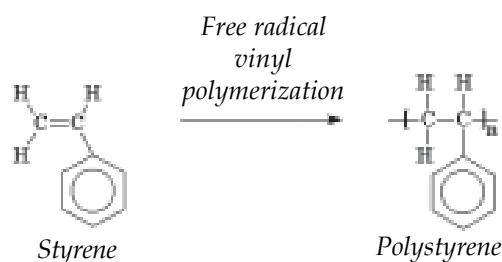
Recently, a new amide based polymer, MXD-6, has been made from meta-xylene diamine and adipic acid. Biaxially oriented film produced from this polymer is used in several packaging applications; it has excellent thermal properties and provides a good barrier to gases and moisture.

Both the melting point and  $T_g$  of MXD-6 are between those of nylon 6 and PET, but MXD-6 has better gas barrier properties than nylon 6 and PET at all humidities, and is better than EVOH at 100% RH, due to the existence of benzene ring in the MXD-6 polymer chain. Together with its

high clarity and good processability, these properties make MXD-6 nylon film suitable as a base substrate of laminate film structures for use in lidding and pouches, especially when the film is exposed to retort conditions.

## Polystyrene

If ethylene and benzene are reacted together with a suitable catalyst, ethyl benzene is formed. Further, a process of dehydrogenation produces styrene (PS). Polystyrene is made by the addition polymerization of styrene.



Polystyrene is a vinyl polymer. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. Polystyrene is produced by free radical vinyl polymerization, from the monomer styrene.

The polymer is normally atactic and is thus completely amorphous because the bulky nature of the benzene rings prevents a close approach of the chains. With the use of special catalysts and polymerization techniques, isotactic PS has been prepared but it reverts to the atactic form on melting. The  $T_g$  is in the range 90-100°C because of the stiffening effect of the benzene ring. This, coupled with the amorphous nature of the polymer, results in a material which is hard, rigid and transparent at room temperature. In this form, it is commonly referred to as crystal grade PS.

There is a new kind of polystyrene, called syndiotactic polystyrene. It is different because the phenyl groups on the polymer chain are attached to alternating sides of the polymer backbone chain. "Normal" or atactic polystyrene has no order with regard to the side of the chain on which the phenyl groups are attached. The new syndiotactic polystyrene is crystalline and melts at 270 °C. This is the polystyrene of the future.

Polystyrene is an inexpensive and hard plastic and it is also made in the form of foam packaging and insulation (Styrofoam is one brand of polystyrene foam). Clear plastic disposable drinking cups used for serving tea and ice creams are made of polystyrene.

Polystyrene makes a distinctly metallic sound when dropped onto a hard surface. It has a high refractive index (1.592), which

gives it a particular high brilliance. Although acids and alkalis have no effect on it, it is soluble in higher alcohols, ketones, esters, aromatic and chlorinated hydrocarbons and some oils. While being a reasonably good barrier to gases, it is a poor barrier to water vapor. To overcome



*Fig. 2.4. Polystyrene based food packaging materials (Disposable thermo formed trays and containers)*

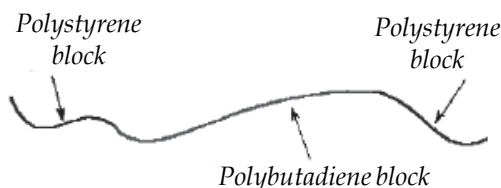
the brittleness of polystyrene, synthetic rubbers can be incorporated at levels generally not exceeding 14% w/w. The rubbers act by restricting propagation of microcracks formed during impact loading. Such a process increases the impact strength and flexibility, but transparency, tensile strength and thermal resistance are much reduced. The chemical properties of this toughened or high impact polystyrene (HIPS) are much the same as those for unmodified polystyrene.

HIPS is an excellent material for thermoforming. Because it is transparent, the use of radiant heat for thermoforming is inefficient and pigmented sheet is often used. It is injection molded into tubes, which find wide use in food packaging, despite being opaque. Crystal grade PS can be made into a film but it is brittle unless the film is biaxially oriented.

The properties of polystyrene that make it useful for many applications as a solid

polymer also make it very desirable as a foam. PS foam has a high modulus, good water resistance, low moisture transmission, ease of fabrication and low cost. Closed cell foams have excellent thermal insulating capability, low weight and good cushioning characteristics. The combination of those properties provides a wide spectrum of products.

*Copolymer of Styrene:* Polystyrene is also a component of a type of hard rubber called poly(styrene-butadiene-styrene) or SBS rubber. SBS rubber is a thermoplastic elastomer. Poly(styrene-butadiene-styrene), or SBS is a hard rubber, which is used for things like the soles of shoes, tire treads, and other places where durability is important. It is a type of copolymer called a block copolymer. Its backbone chain is made up of three segments. The first is a long chain of polystyrene, the middle a long chain of polybutadiene and the last segment is another long section of polystyrene as shown in the picture:



Polystyrene is a tough hard plastic, and this gives SBS its durability. Polybutadiene is a rubbery material, and this gives SBS its rubber-like properties. In addition, the polystyrene chains tend to clump together. When one styrene group of one SBS molecule joins one clump, and the other polystyrene chain of the same SBS molecule joins another clump, the different clumps become tied together with rubbery polybutadiene chains. This gives the material the ability to retain its shape after

being stretched. SBS is also a type of unusual material called a thermoplastic elastomer. These are materials which behave like elastomeric rubbers at room temperature but when heated can be processed like plastics. Most types of rubber are difficult to process because they are crosslinked. But SBS and other thermoplastic elastomers manage to be rubbery without being crosslinked, making them easy to process into nifty useful shapes.

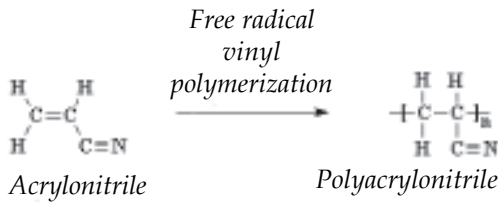
### Acrylonitriles and Associated Copolymers

The ready availability of acrylic acid derivatives from propylene has led to their use in numerous industrial polymer products. Acrylonitrile (sometimes referred to as vinyl cyanide, especially by those who seek to raise fears about the safety of the polymer as a food contact material since the monomer is carcinogenic), b.p. 70°C, is produced mainly by the ammoxidation of propylene.

### Polyacrylonitrile

The polyacrylonitrile polymer (PAN) is 49% nitrile and is an amorphous, transparent polymer. It has a relatively low  $T_g$  (87°C) and provides an outstanding barrier to gas permeation, and exceptional resistance to a wide range of agents. It is not of commercial value in packaging, due largely to its inability to be melt processed. It is therefore copolymerized with other monomers that impart melt processability, thus making its desirable properties available in a packaging form.

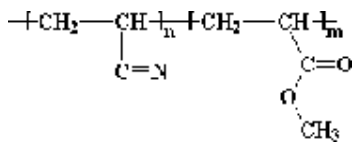
Polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers. It is made from the monomer



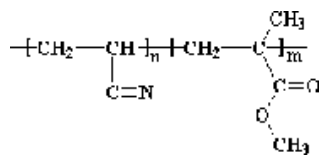
acrylonitrile by free radical vinyl polymerization.

Polyacrylonitrile is used for very few products an average consumer would be familiar with, except to make another polymer, carbon fiber. Homopolymers of polyacrylonitrile have been used as fibers in hot gas filtration systems, outdoor awnings, sails for yachts, and even fiber reinforced concrete. But mostly copolymers containing polyacrylonitrile are used as fibers to make knitted clothing, like socks and sweaters, as well as outdoor products like tents. If the label of some piece of clothing says "acrylic", then it's made out of some copolymer of polyacrylonitrile. Usually, they are copolymers of acrylonitrile and methyl acrylate, or acrylonitrile and methyl methacrylate.

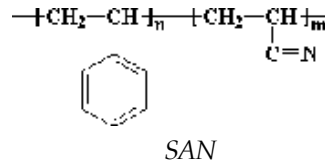
Styrene acrylonitrile copolymer (SAN) is a simple random copolymer of styrene and acrylonitrile. But ABS is more complicated.



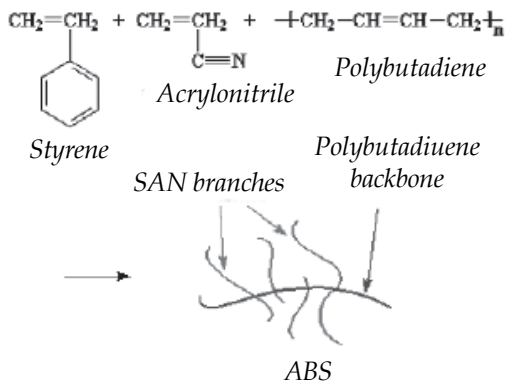
*Poly (acrylonitrile-co-methyl acrylate)*



*Poly (acrylonitrile-co-methyl methacrylate)*



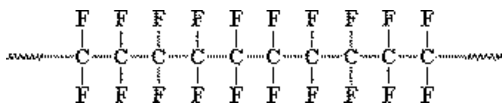
It is made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. Polybutadiene has carbon-carbon double bonds in it, which can polymerize too, which results in a polybutadiene chain with SAN chains grafted onto it, as can be seen below.



Acrylonitrile butadiene styrene (ABS) is a stronger plastic than polystyrene because of the nitrile groups of its acrylonitrile units. The nitrile groups are very polar, so they are attracted to each other. This allows opposite charges on the nitrile groups to stabilize each other. This strong attraction holds ABS chains together tightly, making the material stronger. Also, the rubbery polybutadiene makes ABS tougher than polystyrene.

**Poly (Tetrafluoroethylene) {Poly (Difluoromethylene)} - (PTFE)**

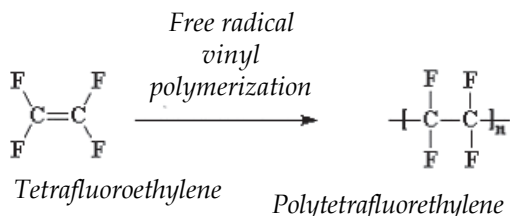
The high thermal stability of the carbon-fluorine bond has led to considera-



ble interest in fluorine-containing polymers. They are set apart from other vinyl polymers because their monomers are the only ones which need not bear any hydrogen on the ethylenic carbons in order to be polymerizable. PTFE was a chance discovery by Plunkett in 1938. Today it accounts for about 80% of the fluorinated polymer produced and is commonly referred to as Teflon.

Polytetrafluoroethylene, or PTFE, is made of a carbon backbone chain, and each carbon has two fluorine atoms attached to it.

Polytetrafluoroethylene is made from the monomer tetrafluoroethylene by free radical vinyl polymerization.



The non-stick nature of PTFE is due to the presence of fluorine atoms in the polymer, which repel other molecules coming close.

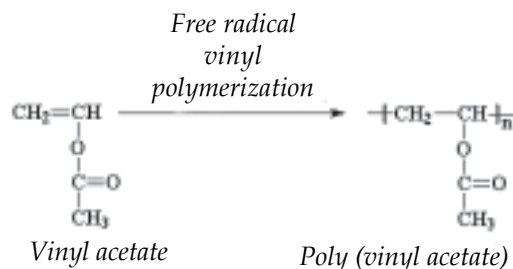
In food packaging, PTFE finds wide use as a non-stick separating surface between thermoplastic films and the jaws of heat sealers. It is common to use a band of PTFE (often reinforced with glass fibers) on continuous heat sealers.

Polytetrafluoroethylene, better known by the trade name Teflon, is used to make non-

stick cooking pans, and anything that needs to be slippery or non-stick. The bond between the fluorine atom and the carbon atom is so strong and stable that nothing reacts with it. Even when it gets as hot as a frying pan, not even oxygen will react with it. PTFE is also used to treat carpets and fabrics to make them stain resistant. What is more, it is also very useful in medical applications. Because human bodies rarely reject it, it can be used for making implants.

### Poly (Vinyl Acetate), or PVA

PVA is a vinyl polymer, made by free radical vinyl polymerization of the monomer vinyl acetate.



Poly (vinyl acetate), or PVA for short, is one of those low-profile behind-the-scenes polymers. One place where PVA can be found is between two pieces of wood that are glued together. PVA is used to make wood glues, as well as other adhesives. Paper and textiles often have coatings made of PVA and other ingredients to make them shiny.

### Ethylene-Vinyl Acetate (EVA)

Ethylene-vinyl acetate (EVA) copolymers with a vinyl acetate (VA) content of 3-12%. They are similar in flexibility to plasticized PVC, and have a good low temperature flexibility and toughness. Their impact strength increases with VA



content and molecular weight. As the VA level increases, EVA becomes less crystalline and more elastic; as the crystallinity decreases, the permeability to gases, moisture, fats and oils increases. The absence of leachable plasticizer provides a clear advantage over plasticizer PVC in some food applications. The addition of antiblocking and /or slip additives reduces sparkle and clarity, and increases haze.

EVA copolymers are not competitive compared to other films because of their high surface tack and friction, which make them difficult to handle on conventional processing machinery. However, they do have three advantages over LDPE; the heat sealing temperature is lower, the barrier properties are lower, and they have excellent stretch properties, the first 50% of extension at room temperature being elastic. Thus they find use as a stretch film for food packaging (particularly fresh meat) and cling-wrap purpose, and are likely to replace PVC for stretch wrapping of foods. EVA is also used in co-extrusion processes for the manufacture of multilayer films.

### **Ethylene-Vinyl Alcohol (EVOH)**

By combining the processability of ethylene polymers with the barrier properties obtained from vinyl alcohol polymers, ethylene-vinyl alcohol (EVOH) copolymers offer not only excellent processability, but also superior barrier to gases, odour, fragrances, solvents, etc. It is these characteristics that have allowed plastic containers containing EVOH barrier layers to replace many glass and metal containers for packaging food. EVOH copolymers were introduced in Japan in the 1970's and in USA in early 1980's.

EVOH resins are hydrolyzed copoly-

mers of vinyl acetate and ethylene. The vinyl alcohol base has exceptionally high gas-barrier properties, but is water-soluble and difficult to process. By copolymerizing ethylene with vinyl alcohol, the high gas-barrier properties are retained, and significant improvements are achieved in moisture resistance and processability.

EVOH copolymers are highly crystalline in nature and their properties are highly dependent upon the relative concentration of the co-monomers. Generally, as the ethylene content increases, the gas barrier properties decrease, the moisture-barrier properties improve, and the resins process more easily.

The most outstanding characteristic of EVOH resins is their ability to provide a barrier to gases. Their use in a packaging structure enhances flavour and quality retention by preventing oxygen from penetrating the package. In those applications where gas-fill packaging techniques are used, EVOH resins effectively retain the carbon dioxide or nitrogen used to blanket the product.

Due to the presence of hydroxyl groups in their molecular structure, EVOH resins are hydrophilic and absorb moisture. As moisture is absorbed, the gas-barrier properties are affected. However, through the use of multilayer technology to encapsulate the EVOH resin layer with high moisture-barrier resins such as polyolefins, the moisture content of the barrier layer can be controlled.

EVOH resins have high mechanical strength, elasticity and surface hardness, very high gloss, low haze, excellent abrasion resistance, very high resistance to oils and organic solvents, and provide an

excellent barrier to odours. When used as the core of a multilayer material, they provide excellent performance.

EVOH resins are the most thermally stable of all the high barrier resins. This stability allows the regrinding and reuse of scrap generated during processing back into the package being produced. Many of the rigid packaging containers being produced today have regrind layers containing up to 15% EVOH.

### Laminates/Co-extruded Films

As can be seen from Table 2.1, no single polymer possesses all the desirable properties that may be required and, as the range of possible applications in the food industry is so diverse, there can be no such thing as the ideal universal packaging material. Optimum properties in each individual case can be achieved by recourse to several polymers and even non-plastic materials such as aluminium or

**Table 2.1. Properties of major packaging resin films**

(Data based on 25  $\mu\text{m}$  thickness)

	LDPE	LLDPE	HDPE	PP	OPP	PVC
Density (g/cc)	0.91– 0.925	0.918– 0.923	0.945– 0.967	0.91	0.90	1.22– 1.36
Yield (m <sup>2</sup> /kg)	42.6	42.5	41.2	44	44	28
Tensile Strength (MPa)	1.5-5	3-8	2.5-6	30-40	20-30	4-8
Tensile modulus (MPa) Secant	20.40	25	125	300	350	350 -600
Elongation at break (%)	200- 600	400- 800	200- 600	200- 350	50- 275	100- 400
Tear strength (elmendorl) (g)	100- 200	150- 900	200- 300	-	340	400- 700
WVTR g/m <sup>2</sup> /day at 38°C & 90% RH gradient	14-18	14-18	5-7	7-9	4	30-40
O <sub>2</sub> Permeability (cc/m <sup>2</sup> /day.atm 25°C)	7000- 8000	7000- 8000	1500- 2000	2000- 3000	2000- 2500	300- 400
Haze (%)	5-10	6-13	3	3	3	1-2
Light transmission (%)	65	-	-	80	80	90
Heat seal temperature range (°C)	120- 175	105- 170	135- 155	95- 150	95- 150	140- 170
Service temperature (°C)	-55 to 80	-29 to 105	-40 to 120	5 to 120	5 to -120	-29 to 65

paper, in combination. Such combinations or laminates, consist of layers of individual materials on top of each other and bonded together by adhesives. Some of the individual resins can also be co-extruded to get the required barrier properties for better shelf life of the food products.

Some of the laminates/co-extruded films available today in the market for food packaging applications with their barrier properties are shown in the Table 2.2.

**ADVANTAGES OF PLASTICS OVER TRADITIONAL PACKAGES**

Many properties of plastics make them ideally suited for food packaging. In most cases, it is a combination of properties that enables plastics to win the battle for adoption in comparison to other traditional packaging materials used in food packaging.

PVDC	IONO-MER	PET	PC	NYLON	OPS	EVA	EVOH
1.6-1.7	0.94-0.96	1.4	1.2	1.14	1.05	0.93	1.14-1.19
24	42.0	28.4	32.5	35	38	41.9	32.7-34.7
8-16	3.5-5	25-33	9-11	25.37	8-12	2-3	1.2-1.7
50-150	10-50	700	320	250-300	400-475	8-20	300-385
50-100	300-600	70-130	100-150	70-120	2-30	500-800	120-280
10-90	20-40	20-100	20-50	15-30	2-15	40-200	400-600
2-4	20-30	21	50-100	150	100-150	20-50	20-50
5-25	7000-8000	50-80	3000	25-40	4000-5000	10000	0-5.2
1-5	1-15	2	1	1.5	1	2-10	1-2
90	85	88	89	88	92	55-75	90
120-150	105-175	135-175	205-215	120-175	120-175	65-205	175-205
-18 to 135	-100 to 165	-75 to 150	-135 to 140	-75 to 205	-60 to 80	-75 to 65	-18 to 50

## Density

Density ranges of 0.9 to 1.4 g/cc are typical for most plastics used in packaging. This density range compares to about 2.6 for glass, 2.7 for aluminum, 0.8-0.9 for paper, 1.5 for polymer coated cellophane, and about 8 for steel. Although metals and glass have higher tensile strength/weight ratios than most common plastics, thickness far greater than required to hold the product from a strength point of view are required to overcome brittleness (glass) or the tendency to bend and buckle (metals). Thus the required weight of the rigid container made of plastic is several-fold less than for metal or glass.

Paper is a lightweight material, but its wet strength is so low that it cannot qualify for many foods packaging applications unless it is combined with plastic for reinforcement and waterproofing.

Ability of plastics to provide lightweight packages, which is an important consumer convenience and a way for processors to reduce shipping cost, is probably the largest single driving force behind plastics penetration into the market for food containers that were once the exclusive province of metal and glass.

## Break Resistance

In the thin gauges commonly used in

**Table 2.2. Barrier Properties of Flexible Packaging Materials**

Packaging materials	Thickness (µm)	WVTR*	OTR**
<b>Laminates:</b>			
PET/LDPE	12/37	9.5	75
LD//PA/EAA	37/25/50	7.2	85
MET.PET/LDPE	12/37	1.5	4
PET/HDPE-LDPE	12/112	3.3	70
MET.PET/HDPE-LDPE	12/112	0.6	2
PET/LDPE/EAA	12/25/25	6.4	70
HDPE/EAA	25/25	3.8	1395
PAPER/FOIL/LDPE	40/9/37	nil	nil
PET/FOIL/LDPE	12/9/10	nil	nil
PET/PP	12/50	3.5	6.5
PET/FOIL/PP	12/12/50	nil	nil
<b>Co-extruded Films:</b>			
LDPE/LLDPE	50	9	4000
LDPE/HDPE	120	2.0	1500
HDPE/LDPE/HDPE	110	2.0	1200
HDPE/LDPE/EAA	110	2.1	1500
LDPE/BA/PA/BA/EAA	90	5.4	85
CPP/BA/PA/BA/EAA	90	4.1	80
* g/m <sup>2</sup> /24 h at 38°C and 90% RH gradient.			
** cc/m <sup>2</sup> /24h atm at 27°C and 65% RH.			

packaging, rigid plastics containers resist breaking far more effectively than glass. This, along with low density, is the major reason why plastics have taken so many rigid packaging applications away from glass, which is otherwise an excellent packaging material from the food protection standpoint.

### Sealability

All flexible packages must be closed in some way, and the vast majority of them are closed by heat-sealing, a process in which a coating on the flexible substrate is heated in the packaging machinery until it melts and then is held in contact with the similarly coated opposite surface until the two coatings solidify, as one layer. Polymer coatings and adhesives are universally used to perform this function.

No other packaging material can match plastics ability to create strong hermetic seals at low temperatures (100-250°C). Some resins have even been developed that provide an excellent seal in the presence of liquids, greases and powders. EAA and octene based LLDPE are excellent materials for sealability.

### Fabrication Flexibility

All types of common plastics can be readily converted into thin, strong and clear films. This means that for thousands of flexible packaging applications, metal and glass cannot be used and only paper, glassine, and cellophane can compete. Plastics are unsurpassed in the ease with which special shapes can be readily created. This attribute is particularly important for rigid containers, where imaginative design is constantly providing ever more consumer friendly packages that

perform useful functions not yet fully capitalized on this important attribute; future growth of plastics in rigid packaging will depend more and more on designers and fabricators learning how versatile plastics can be in providing consumer-friendly packages.

### Impermeability to Gases

Many food products are sensitive to attack by water vapour and oxygen. For example, crackers become soggy on high-humidity days, and fat in food turns rancid when exposed to oxygen.

Glass, metal and pinhole-free aluminum foil (the latter a rarity) are totally impermeable to these two gases which deteriorate so many food products. Plastics and polymer-coated cellophane rank well below these materials but they are far more impermeable than uncoated paper. Even simple, uncoated, homopolymer plastics such as polyethylene and polypropylene have sufficient moisture barrier property for many applications. The early development of thin plastic barrier coatings applied to these low cost films provided a moisture barrier that was totally adequate in most cases.

Incorporating an oxygen barrier in all-plastic flexible package can be accomplished by including a barrier plastic layer in a multilayer construction. In the case of rigid containers, this is more complicated task, but recent developments in extruded barrier polymers and co-extrusion technology have allowed plastics to penetrate the rigid packaging market for some oxygen-sensitive food applications. Although all-plastic packages will never have the infinite oxygen barrier provided by metal and glass, still they are now close to

providing enough oxygen barrier so that in time, this factor alone will not disqualify all-plastic flexible and rigid packages from competing for all the food packaging applications.

Also, plastic with controlled permeability to gases becomes a positive attribute in the design of packages for products such as fresh produce, which continue to respire after being harvested. Briefly, the shelf life of these products can be greatly extended if they are packaged in a material which is selectively permeable to O<sub>2</sub> and CO<sub>2</sub> and can thus maintain an optimum O<sub>2</sub>/CO<sub>2</sub> ratio in the atmosphere surrounding the product.

Plastic packages with controlled, selective gas permeability are just beginning to be used in food packaging, but one day they will offer an important way of preserving fresh food for periods far longer than is now possible. This property of selective permeation cannot be provided by metal, glass and aluminium foil.

### **Light Control and Package Appearance**

Unmodified plastic films and sheets range in appearance from crystal clear to hazy. Pigments or soluble dyes can be added to produce total opacity in virtually any colour or to produce transparent coloured films and sheets. This enormous versatility gives the package designer freedom to create a package that clearly displays the contents. If the food being packaged is sensitive to light-catalyzed oxidation, as many foods are, pigmentation or metallization can be used to screen out light and to provide a background against which artistically designed graphics are

revealed to their best advantage. No other packaging material offers package designers such a wide range of choices. Many flexible packaging convectors are successful mainly because they are experts in exploiting plastics versatility in this area.

### **Tear and Puncture Resistance**

This attribute gives plastics a major edge over paper, cellophane and aluminum foil in flexible packages. In addition, most plastics films are more resistant than aluminum foil to cracking when subjected to repeated flexing.

### **Low Temperature Flexibility**

Plastic films remain flexible at low temperatures, whereas cellophane starts to embrittle below about 4°C. This low temperature flexible characteristics of plastics was major factor in their displacing many flexible cellophane packages.

### **Metal Coating Receptivity**

Very thin coatings of aluminum can be readily vapour deposited on plastic substrates in high vacuum chambers. The resulting attractive product is less expensive and sometimes functionally superior to aluminum foil, which is sealed into flexible packages to provide a barrier to light, moisture, and oxygen.

### **Print Receptivity**

The use of package to advertise and describe the product is an exceedingly important food marketing tool. Paper and cellophane are marginally superior to plastic in their print receptivity, since some plastics require an inexpensive pre-treatment to develop this attribute whereas the former materials do not. This difference no longer gives paper or cellophane

any significant advantage over plastic. By contrast, metal and glass containers are more difficult to print and usually require expensive application of paper labels to carry the graphics.

### BIBLIOGRAPHY

- Becker K, Koszinowski J and Piringer O (1983). Permeation von Riechund Aromastoffen durch Polyolefine. *Deutsche Lebensmittel-Rundschau*, 79: 257-266.
- Brown WE (1992). *Plastics in Food Packaging Properties, Design and Fabrication*. Marcel Dekker Inc., New York.
- Crosby NT (1981). *Food Packaging Materials (Aspects of Analysis and Migration of Contaminants)*. Applied Science Publishers Ltd, London
- Jenkins WA and Harrington JP (1991). *Packaging Foods with Plastics*. Technomic Publishing Co. Inc, Lancaster, Pennsylvania.
- Koszinowski J and Piringer O (1986). Influence of the packaging material and the nature of the packed goods on the loss of volatile organic compounds-permeation of aroma components. In: *Food Packaging and Preservation*, ed: Mathlouthi M. Elsevier Applied Science Publishers, London, pp. 325-340.
- Paine FA and Paine HY (1982). *A Handbook of Food Packaging*, The Council of the Institute of Packaging, Leonard Hill, Glasgow, UK.
- Robertson GL (1993). *Food Packaging: Principles and Practice*. Marcel Dekker Inc, New York.

