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Contemporary approaches to improvement of polyolefin barrier properties

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Bakalářská práce bude zaměřena na současný stav ve zlepšování bariérových vlastností polyolefinů. Bude pokrývat pět hlavních oblastí:
Polyolefiny v obalářství
Zpracování polyolefinových fólií a desek
Fyzikální vlastnosti polyolefinových obalů
Konvenční přístupy ke zlepšování bariérových vlastností
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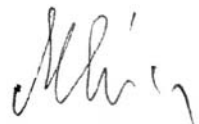   Ústav inženýrství polymerů

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ABSTRAKT

Bakalářská práce pojednává o výrobě a zpracování obalových prostředků z polyolefinů, jejich fyzikálních vlastnostech, použití a obecně o současných přístupech ke zlepšování bariérových vlastností polyolefinových obalů. Jsou zde popsány jednotlivé polymery, z nichž se bariérové obaly skládají i způsoby zpracování fólií a desek na obalové materiály. Dále je věnována pozornost použití těchto materiálů a současným trendům ve světě obalových technologií.

Klíčová slova: Polyolefiny, obaly, zpracování, fólie, desky, vícevrstvé a bariérové obaly

ABSTRACT

The Bachelor thesis directs towards manufacturing and processing of polyolefin or polyolefin-based packaging materials, their physical properties, utilization and, in general, recent trends in the improvement of their barrier properties. Individual polymers and processing technologies used in packaging are described. Special attention is paid to contemporary trends and inovations in polyolefin packaging.

Keywords: Polyolefins, packaging, processing, films, sheets, multilayers, barrier layers

Motto: Když si člověk postaví dům, vždycky zpozoruje, že se při tom naučil něčemu, co měl rozhodně znát, než začal stavět.

<div align="right">Friedrich Nietzsche</div>

Rád bych poděkoval za pomoc Ing. Romanu Čermákovi, Ph.D. za vstřícný přístup a pomoc při sestavování této práce.

Souhlasím s tím, že s výsledky mé práce může být naloženo podle uvážení vedoucího bakalářské práce a ředitele ústavu. V případě publikace budu uveden jako spoluautor.

Prohlašuji, že jsem na celé bakalářské práci pracoval samostatně a použitou literaturu jsem citoval.

Ve Zlíně, 21. 05. 2007 ....

<div align="center">podpis</div>

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INTRODUCTION

Polyolefin-based polymers, polymer blends and composites are popular nowadays because of their versatility of use and balanced properties. Various materials like wood, paper, glass or metals are being replaced by plastics because these are much cheaper and often easy to process, while maintaining desired physical properties. Most of the packaging materials are either purely polyolefinic or polyolefin based and polyolefins are presently the most used polymer materials in common. Their importance in our lives increases as we are getting used to foods, beverages and other goods in plastics packaging, which takes less space, is usually tough enough to withstand even harsh handling and presents good protection and shelf life, so best before date look more pleasant and does not bind us to consume or use the product early.

As can be seen, packaging industry and barrier sheets and films production extends continuously and every day there can be something new invented, so a complete objective observation cannot be done. A purpose of this thesis is to summarize some interesting facts about this wide field of plastics use

The purpose of this work is to present contemporary view of packaging industry, most common processing methods, properties of these materials and finally barrier properties of packaging and ability to keep packed product fresh and safe for a maximum time possible.

First chapter focuses on basic polyolefins which are commonly used in packaging industry. They present either single packaging material (like LDPE sacks) or participate a multi-layer composition, where various layers of polymers lay one on another to provide desired protection, because every polymer has its own benefits.

The second chapter is about processing of the materials. An employment of traditional methods of polymer processing in packaging production is described.

Third chapter concludes characteristics of polymers giving insight into their physical properties.

The last two chapters summarize recent trends and approaches to improve properties of the packaging. Because these methods develope continuously, there are always arising new possibilities to improve the packaging, make them cheaper and make our lives easier.

1 POLYOLEFINS IN PACKAGING

Ever-evolving packaging film technologies strive to deliver product protection, food safety, quality retention and ultimately, consumer satisfaction, to the meat, poultry, and prepared food industries.

Nearly all used packaging films and sheets are based on polyolefins because of their reduced price and moderate physical properties. A disadvantage of polyolefin films is its permeability which means that polyolefins layer by itself have low barrier properties for gasses for instance. Solution of this problem is an addition of high-barrier layer like Ethylene-vinylalcohol (EVOH) copolymer or polyamide (PA) which provides necessary gas or moisture barrier. Packaging films then appear as multilayer structures with polyolefin base and additional barrier layers. Polyolefin film usually makes outer layers because of protection of high-barrier layers in the middle and provides an adhesion possibility for attaching these films to containers which might not be possible when using bare barrier layers (PA).

1.1 Polyolefins

Olefin, which means oil-forming, is an old synonym for alkene, and was, originally, the name given to ethylene. Alkenes are hydrocarbons containing carbon-carbon double bonds, such as ethylene and propylene. In the plastics industry, olefin is a common term that refers to the family of plastics based on ethylene and propylene. The term polyolefin strictly applies to polymers made of alkenes, whether homopolymers or copolymers. It includes the family of polyethylene, and the family of polypropylene [1].

More specific type of olefin is a poly-alpha-olefin (or poly-α-olefin, PAO), a polymer made by polymerising an alpha-olefin. It is an alkene where the carbon-carbon double bond starts at the α-carbon atom, i.e. the double bond is between the #1 and #2 carbons in the molecule. Common alpha-olefins used as co-monomers to give a polymer alkyl branching groups.

Fig. 1.1 - 1-hexene, an example of an alpha-olefin

These alkyl groups, shaped in numerous conformations, make it difficult for the polymer molecules to line up orderly so they do not crystallize or solidify easily and are able to remain oily, viscous liquids even at lower temperatures (synthetic motor oils).

1.2 Polyethylene family

Polyethylene (PE) is a family of polymers based on ethylene. Polyethylene can be linear or branched, homopolymer or copolymer. In the case of a copolymer, the other comonomer can be an alkene such as propene, butene, hexene or octene or a compound having a polar functional group such as vinyl acetate (VA), vinyl alcohol (VOH), or ethyl acrylate (EA). Figure 1.2 presents a diagram of the family of polymers based on ethylene monomer.
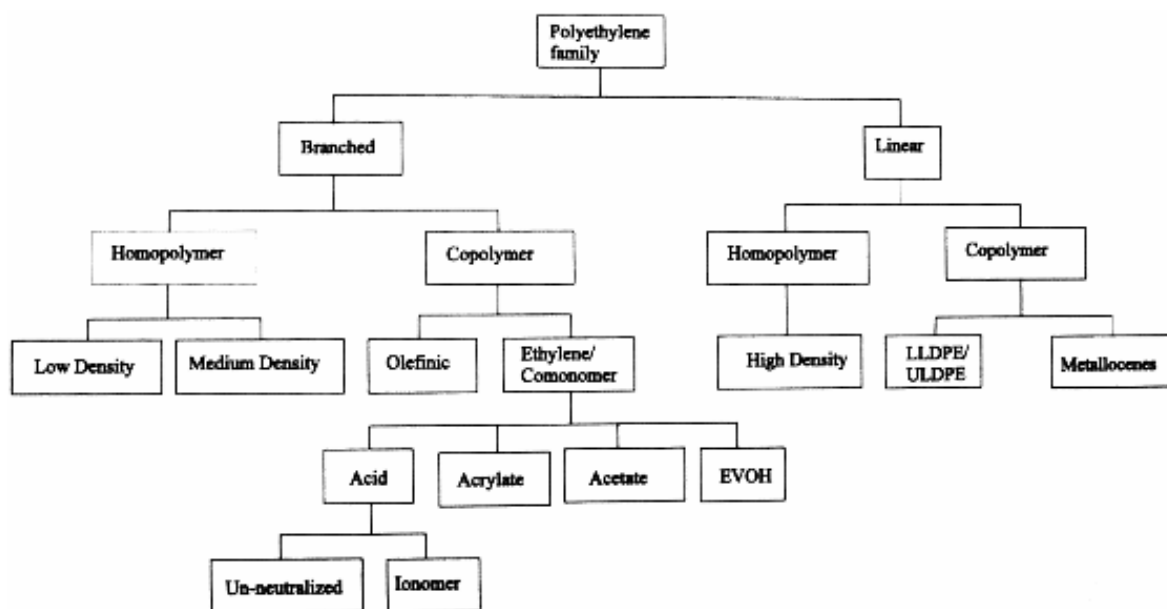
Fig. 1.2 – Polyethylene family

1.3 Branched polyethylenes

The family of branched polyethylenes includes homopolymers and copolymers of ethylene that are non-linear, thermoplastic, and partially crystalline. They are fabricated under high pressure and temperature conditions by a free radical polymerisation process. Backbone length, side chain length and branching vary. Branched PE has lower crystallinity and consequently lower density than the linear type, so is known as low density PE (LDPE). LDPE typically has a crystallinity of 40 to 60 %, with a density of 0.910 to 0.940 g/cm^3; in contrast, HDPE has a density of about 0.940-0.970

g/cm^3. Comonomers such as propylene and hexene are commonly used in the reaction to help control molecular weight [1].

1.3.1 Low density polyethylene

The backbone consists of ethylene groups with side-chains:

$$
\left[\begin{array}{cc} \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} & \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} \end{array}\right]_n
$$
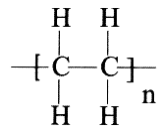
The chain branching in homopolymer LDPE gives this polymer a number of desirable characteristics such as clarity, flexibility, heat sealability and ease of processing. The actual values of these properties depend on the balance between the molecular weight, molecular weight distribution, and branching.

LDPE is also versatile with respect to processing mode, and is adaptable to blown film, cast film, extrusion coating, injection moulding, and blow moulding. Film is the single largest form of LDPE produced. Products made of LDPE include containers and bags for food and clothing, industrial liners, vapour barriers, agricultural films, household products, and shrink and stretch wrap films. LDPE is the most widely used plastics in packaging.

The major competitor to LDPE is LLDPE, which provides superior strength at equivalent densities. However, LDPE is still preferred in applications demanding high clarity or for extrusion coating a substrate. Ethylene can be copolymerized with alkene compounds or monomers containing polar functional groups, such as vinyl acetate and acrylic acid. Branched ethylene/alkene copolymers are essentially the same as LDPE, since in commercial practice a certain amount of propylene or hexene is always added to aid in the control of molecular weight [1].

1.3.2 Ethylene Vinyl Acetate

Ethylene vinyl acetate copolymers (EVA) are produced by copolymerising ethylene and vinyl acetate monomers:

$$
\begin{array}{cc}
H & H \\
| & | \\
C = C \\
| & | \\
H & O \\
 & | \\
 & C = O \\
 & | \\
 & CH_3
\end{array}
$$
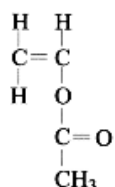
The result is a random copolymer, where

$$
-O - \underset{\underset{O}{\|}}{C} - CH_3
$$
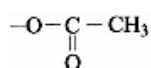
groups appear as side groups at random locations on the carbon chain, replacing H atoms.

EVA copolymers with VA contents ranging from 5 % to 50 % are commercially available, 5 % to 20 % is recommended. EVA resins are mainly recognized for their flexibility, toughness, and heat sealability.

Because of its excellent adhesion and ease of processing, EVA is often used in extrusion coating and as a coextruded heat seal layer. Examples include functioning as a heat sealing layer with polyethylene terephtalate (PET), cellophane and biaxially oriented polypropylene (PP) packaging films (20 % VA) for cheese wrap and medical films. Because EVA has limited thermal stability and low melting temperature, it has to be processed at relatively low temperatures. However, this also results in toughness at low temperatures, which is a significant asset for packages such as ice bags and stretch wrap for meat and poultry [1]. EVA copolymers are widely used as Hot Melt adhesives.

1.3.3 Ethylene Acrylic Acid

The copolymerization of ethylene with acrylic acid (AA)

$$
\begin{array}{cc}
H & H \\
| & | \\
C = C \\
| & | \\
H & C = O \\
 & | \\
 & OH
\end{array}
$$
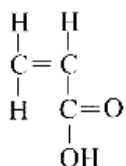
produces copolymers containing carboxyl groups (HO-C=0) in the side chains of the molecule. These copolymers are known as ethylene acrylic acid (EAA). They are flexible thermoplastics with chemical resistance and barrier properties similar to low density polyethylene (LDPE). EAA, how-
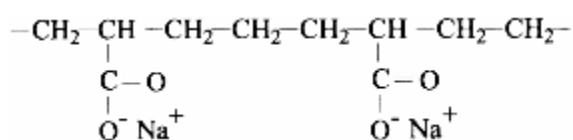
ever, is superior to LDPE in strength, toughness, hot tack and adhesion, because of the increased intermolecular interactions provided by the hydrogen bonds. Major uses include blister packaging and as an extruded tie layer between aluminium film and other polymers.

As the content of AA increases, the crystallinity decreases, which implies that clarity also increases. Similarly, adhesion strength increases because of the increase in polarity, and the heat seal temperature decreases due to the decrease in crystallinity.

Films of EAA are also used in flexible packaging of meat, cheese, snack foods, and medical products; in skin packaging; and in adhesive lamination. Extrusion coating applications include condiment and food packages, coated paperboard, aseptic cartons, composite cans and toothpaste tubes. Food and drug assessment (FDA) regulations permit use of up to 25 % acrylic acid for copolymers of ethylene in direct food contact [1].

1.3.4   Ionomers

Neutralization of EAA or a similar copolymer, for example ethylene methacrylic acid (EMAA), with cations such as Na^+, Zn^{2+}, Li^+, etc., produces a material that has better transparency and toughness, and higher melt strength than the un-neutralized copolymer. These materials are called ionomers because they combine covalent and ionic bonds in the polymer chain. The structure of an ionomer of the ethylene sodium acrylate type is:

$$-CH_2-\underset{\underset{\underset{O^-Na^+}{|}}{\overset{|}{C-O}}}{CH}-CH_2-CH_2-CH_2-\underset{\underset{\underset{O^-Na^+}{|}}{\overset{|}{C-O}}}{CH}-CH_2-CH_2-$$

Ionomers were developed in 1965 by R. W. Rees and D. Vaughan, while working for DuPont, which uses the trade name Surlyn™

Barrier properties of ionomers alone are relatively poor, but combined with poly vinylidene chloride (PVDC), high density polyethylene (HDPE), or film they produce composite materials that are excellent barriers.

Ionomers are frequently used in critical coating applications, films, and laminations. Applications include heat seal layers in a variety of multi-layer and composite structures. They are used in combination with nylon, PET, LDPE, and PVDC. Coextrusion lamination and extrusion coating are the most common processing techniques.

Ionomers are used in packaging where formability, toughness, and visual appearance are important. Food packaging films are the largest single market. They are highly resistant to oils and aggressive products, and provide reliable seals over a broad range of temperatures. Ionomers stick very well to aluminum foil. They are also used extensively as a heat-sealing layer in composite films. Other applications of ionomers include frozen food (fish and poultry), cheese, snack foods, fruit juice (TetraPak™ type container), wine, water, oil, margarine, nuts, and pharmaceuticals. Heavy gauge ionomer films are used in skin packaging for hardware and electronic products due to their excellent adhesion to corrugated board and excellent puncture resistance. Sodium can be replaced by other metals such as zinc, and other comonomers such as methacrylic acid can be used. There are more than fifty commercial grades of ionomer with a wide range of properties. In general, sodium ion types have better optical properties, hot tack and oil resistance. Zinc ionomers are more inert to water, and have better adhesion properties in coextrusion and for extrusion coating of film [1].

1.4 Linear Polyethylenes

High density polyethylene is the second most widely used packaging plastics. It has a nearly totally linear structure. This results in a greater ability to crystallize, producing a tighter packing of molecules and consequently a higher density.

Linear polyethylenes have traditionally been produced using a Ziegler-Natta stereospecific catalyst. These new catalysts, which only allow the combination of free radicals in a specific orientation, allowed the density to be increased to 0.97 g/cm^3. Ziegler-Natta catalyst technology allows control over the density through the percentage of comonomer incorporated into the backbone. Since the reactions are run at relatively low temperatures and pressures, the hydrogen abstraction reactions responsible for the branching in LDPE do not occur to any significant extent. The milder reaction conditions also facilitate improved control over the average molecular weight and the molecular weight distribution.

Linear polyethylenes can be divided into the following groups, with density given in parentheses:

ULDPE - ultra low density PE (0.89-0.915 g/cm^3)

LLDPE - linear low density PE (0.916-0.940 g/cm^3)

HDPE - high density PE (0.940-0.965 g/cm^3)

HMW-HDPE – high molecular weight HDPE (0.940-0.965 g/cm^3)

The molecular weight of linear polyethylene ranges from medium to ultra high molecular weight, as shown in Table 1.1 [1].

Table 1.1 - Average molecular weight table for PE

Medium Molecular Weight	<110,000
High Molecular Weight	110 000-250 000
Very High Molecular Weight	250 000 - 3 500 000
Ultra High	>3 500 000

1.4.1   High Density Polyethylene

High density PE is a milky-white, nonpolar, linear thermoplastic material. Its density ranges from 0.940 to 0.965 g/cm^3, and it has a melting temperature of about 128-138 °C. It is one of

the most versatile polymers, and is the second most commonly used plastics in the packaging industry. Typical applications include:

- Containers for milk, detergent, bleach, juice, shampoo, water, and industrial chemical drums made by extrusion blow moulding, buckets, thin walled dairy containers, and closures made by injection moulding;

- Cosmetic containers, pharmaceutical bottles, and deodorant containers made by injection blow moulding;

- Blown and cast films utilized in flexible packaging applications such as cereal, cracker and snack food packaging, wrap for delicatessen products, and produce bags.

Environmental stress cracking is a common problem for high-density polyethylene. It can be defined as the failure of a material that is under stress and exposed to a chemical substance, in conditions where exposure to either the stress alone or the chemical alone does not cause failure. Products such as laundry detergent are known stress-crack agents. In food products, fatty acids can also lead to stress cracking, but it is not as severe as with detergents. A high degree of crystallinity increases the tendency for environmental stress cracking. Therefore, copolymer HDPE is employed for applications such as detergent bottles. The comonomer reduces crystallinity by disrupting the close packaging of the linear molecular chains, and thereby gives greater resistance to crack propagation [1].

1.4.2   Linear Low Density Polyethylene

As mentioned above, linear polyethylene can be produced as a homopolymer, resulting in high-density polyethylene, HDPE, or as a copolymer having as comonomer alkenes such as butene, hexene and octene.

butene $H_2C = CH\ CH_2\ CH_3$

hexene $H_2C = CH(CH_2)_3\ CH_3$

octene $H_2C = CH(CH_2)_5\ CH_3$

The presence of a comonomer in the polymerisation process, when a stereo-specific catalyst is used, results in the production of a rather linear polymer with very short branch-like pendant groups. This polymer is called linear low-density polyethylene (LLDPE) or ultra low-density polyethylene (ULDPE), depending on the density achieved by the addition of the comonomer. The larger the amount of comonomer added, the lower is the density of the copolymer. Normally the amount of comonomer ranges from 1 to 10 %.

Typical uses for LLDPE include stretch/cling film, grocery sacks, and heavy duty shipping sacks. LDPE and LLDPE are often blended to optimise the benefit obtained from both materials, with LLDPE adding strength and LDPE adding heat seal and processability [1].

1.5   Polypropylene

Polypropylene is a thermoplastic material produced by polymerisation of propylene, and has the following structure:

$$-\ (\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}})_n\ -$$
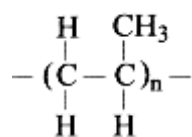
Polypropylene is commercially available as both PP homopolymer, and PP random copolymer, which is produced by the addition of a small amount of ethylene during the polymerisation process. Thermoplastic PP polymers are characterized by low density (0.89-0.92 g/cm^3) and good resistance to chemicals and to mechanical fatigue, including environmental stress cracking. There are a wide variety of applications for PP, from automobile parts to packaging film and containers. Manufacturers of PP continuously are offering PP grades with improved or modified properties [1].

1.5.1 PP Homopolymer

There are isotactic, syndiotactic and atactic versions available.

Isotactic PP, the most common commercial form of PP, is synthesized using Ziegler-Natta catalysts under controlled conditions of temperature and pressure. It forms a highly crystalline material, resulting in good solvent and heat resistance.

Films, which can be produced by both blown and cast methods, can be oriented to provide improved optical characteristics and better strength. Because of the rapid crystallization of PP, blown films must be produced by either water quench or mandrel quench processes, unlike PE, which is cooled by air.

PP is an excellent moisture barrier, and has medium transparency. PP is commonly oriented to improve optical, mechanical, and barrier properties [1].

1.5.2 Random Copolymer Polypropylene

Random copolymer PP typically contains 1.5 to 7 % ethylene, by weight, as a comonomer. The polymer structure is similar to that of isotactic PP with the addition of random insertion of ethylene groups.

Random copolymers show good chemical resistance to acids, alkalis, alcohols, and to low-boiling hydrocarbons, but are not suitable for packaging aromatic hydrocarbons. Moisture-barrier properties are good. For example at 38 °C and 90 % RH, permeability to water vapour can be 235 g $\mu m/m^2$ 24h.

PP random copolymers are processed mainly by blow moulding, extrusion, and injection moulding. Applications include medical packaging, packaging for clothes, and packaging for bakery products and other foods.

Unoriented random PP copolymer films are soft and are easy to heat seal. Applications for oriented PP include shrink wrap (records, toys, games, hardware items, frozen foods and cigarette wrap). A 7 % ethylene copolymer is often used as a heat-seal layer in food packaging [1].

1.6 Polyvinyl Alcohol

Polyvinyl alcohol (PVOH) has the following structure:

$$-(CH_2-CH)_n-$$
$$| \atop OH$$
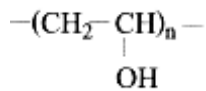
PVOH is produced by hydrolysis of polyvinyl acetate, PVA. The resulting material is amorphous at first, since PVA is amorphous, but it tends to crystallize when oriented. PVOH is atactic, but since the -H and -OH are isomorphous groups, this does not interfere with crystallization. Strong intermolecular forces are imparted by the OH groups with their ability to hydrogen bond. The forces are so strong that PVOH cannot be melt-processed, since its decomposition temperature is below its melting temperature. Without stress, the molecules, though they have a strong tendency to crystallize, are not able to do so because they lack the mobility to rearrange into a crystalline structure.

PVOH has excellent barrier properties to oxygen and many other substances, because of its crystallinity and strong intermolecular forces. In its pure form, however, it is water-soluble. Since the water solubility is imparted by the OH groups. The more acetate groups that are retained, the lower is the water solubility of the PVOH, as well as the less effective the barrier properties.

Because of its extreme water sensitivity and difficulty in processing, PVOH has few packaging applications. Some important markets include packaging for toxic chemicals, such as pesticides, which can be encapsulated in PVOH pouches and placed, package and all, in the mixing tank. The PVOH dissolves, freeing the chemical, which can then be sprayed as usual. PVOH biodegrades in the environment, and does not present problems such as clogging spray nozzles or otherwise interfering with the application of the chemicals. In a similar approach, PVOH is sometimes used for bags for soiled linen in hospitals. The bags and linen can be placed directly in the washer, where the bags dissolve, and thus hospital personnel are able to avoid handling contaminated items [1].

1.7 Ethylene Vinyl Alcohol

Ethylene vinyl alcohol (EVOH) is produced by a controlled hydrolysis of ethylene vinyl acetate copolymer. The hydrolytic process transforms the vinyl acetate group to vinyl alcohol, in a manner analogous to production of polyvinyl alcohol.

For packaging applications, the most important characteristic of EVOH is its outstanding O_2 and odour barrier properties. Packaging structures with EVOH provide high retention of flavours, and

prevent quality loss associated with reaction of oxygen with the product. EVOH also provides a high resistance to oils and organic vapours. This resistance decreases somewhat as the polarity of the penetrating compound increases. For example, the resistance to linear and aromatic hydrocarbons is outstanding, but for ethanol and methanol is low; it may absorb up to about 12 % of ethanol.

The lower the amount of ethylene, the better is the barrier - when the polymer is dry. The lower the percentage of ethylene, the greater is the moisture sensitivity, and the difficulty of processing. EVOH resins are melt-processable, and exhibit high strength, toughness, and clarity. For these reasons, EVOH resins are often the best choice for applications where excellent barrier is required, as long as exposure to moisture can be controlled.

As indicated above, the hydroxyl group, -OH, makes the polymer hydrophilic, attracting water molecules. The presence of water decreases the oxygen barrier properties of the material. Because of its moisture sensitivity, EVOH is usually incorporated into package structures as a buried inner layer in a coextrusion, surrounded by polyolefins or other good water vapour barrier polymers. EVOH can be extruded in films, blow-moulded, or injection-moulded. It can also be processed by coextrusion or lamination, in combination with PE, PP, PET, nylons, and other resins. Applications in packaging include flexible structures and rigid containers, as shown in Table 1.2 [1].

Table 1.2 – Application of EVOH

Processing Method	Sample application	Sample structure
Cast coextrusion	Processed meals, cheese	PET/EVOH/EVA
Blown coextrusion	Red meal	LLDPE/EVOH/LLDPE
lamination	Condiments	OPP/EVOH/LDPE
Coextrusion coating	Aseptic packaging	LDPE/paperboard/EVOH/lonomer
Thermofonming	Yogurt	PP/EVOH/PP
Coextrusion blow molding	Ketchup	PET/EVOH/PET

1.8   Cyclic Olefin Copolymers

Cyclic olefin copolymers (COC) are copolymers of ethylene and norbornene (2,2,1 bicycloheptane), made using metallocene catalysts. They are amorphous polymers, with excellent clarity, low density, and high strength and stiffness, they are predominantly stiff and brittle (see figure 1.3), resistant against acids and bases and has low water absorption [1],[2].
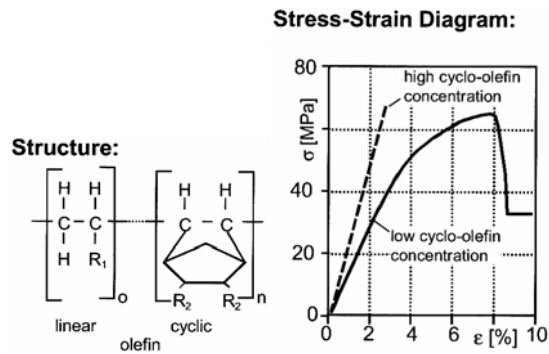
Fig. 1.3 – Characteristics of COCs

Uses for COCs include blister packaging for pharmaceuticals, food packaging, and non-packaging applications. They are reported to be easily metallized, and processable by injection moulding, film extrusion, blow moulding, and thermoforming. Blends and coextrusions of COCs with other materials, including LLDPE and EVOH, are also of interest.

While these materials are still relatively new in terms of commercial availability, they may provide advantages in downgauging due to their excellent stiffness and water vapour barrier characteristics. Their glass-like transparency is also a significant advantage. A broad range of glass transition temperatures can be provided, depending on the norbornene content. Increasing the norbornene levels increases stiffness, strength, T_g, and heat deflection temperature [1].

2   PROCESSING OF POLYOLEFIN FILMS AND SHEETS

In nearly all applications of plastics in packaging, the first step is to convert the solid plastics, usually in pellet or cut scrap form, into a melt, which is going to be shaped using heat and pressure into some useful form, mostly films and sheets of flat or round (bubble). The equipment used to do this is an extruder. It is used directly for film and sheet, and it is part of a blow moulder for bottles, and of an injection moulding machine for injection-moulded or injection blow-moulded packaging. The extruders used in all of these applications work in a similar manner - the purpose of an extruder is to use heat, pressure, and shear to transform the solid plastics into a uniform melt, for delivery to the next stage of processing. This frequently involves mixing in additives such as colour concentrates, blending resins together, and incorporating regrind materials. The final melt is uniform in temperature and in composition and is extruded through a die of particular shape and directions. Specific types of extrusion are described further. Because single screw extruders are often not very good mixers, another mixing systems may be needed.
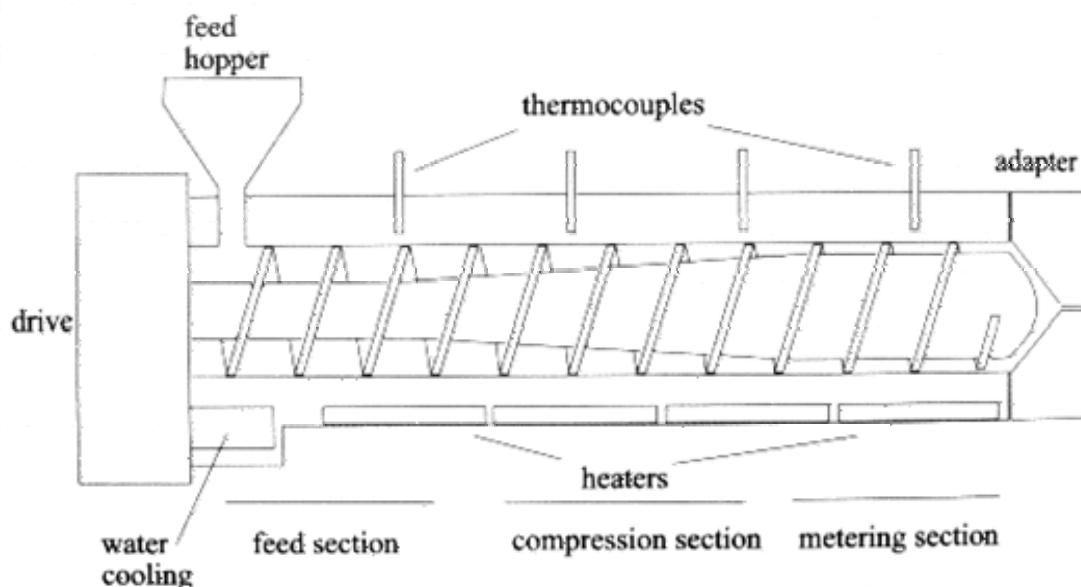

Fig. 2.1 – Extruder

A single-screw or double-screw extruders are used according to heat and mechanical properties of extruded polymer or blend and to properties of die or other additional attached machinery. Screws and barrels have different shapes, lengths and layouts [1],[3].

2.1 Cast Film and Sheet

For the production of cast film or sheet, the melted plastics leaves the extruder through a slit-shaped die, producing a rectangular profile with the width much greater than the thickness. The processes for manufacturing of cast film and cast sheet are essentially identical. Film is differentiated from sheet by its relative stiffness or flexibility, with no clear line between them. Materials with thickness of 0.08 mm or less are considered film, and materials with thickness of 0.25 mm or greater are considered sheet. Between these values, materials are considered film if they are relatively flexible, and sheet if they are relatively rigid. The usual method of producing thin cast film is the cold cast or chill roll process [1] .

2.1.1 Cold Cast and Chill Roll Cast Process

Cast film is generally produced by downward extrusion of the melt onto chilled chrome rollers, which are highly polished to impart good surface characteristics to the film, as shown in Figure 2.2. The first chill roll typically operates at a temperature of at least 40 °C, with subsequent rolls operating at successively lower temperatures to cool the film enough that it can be trimmed and wound. An air knife is typically used only to pin the plastics against the first chill roll. The film dimensions are controlled primarily by the die dimensions, extrusion rate, and take-off speed. Film produced in this manner is characterized by good transparency and stiffness, and output rates are typically higher than for quench tank cooled film [1].
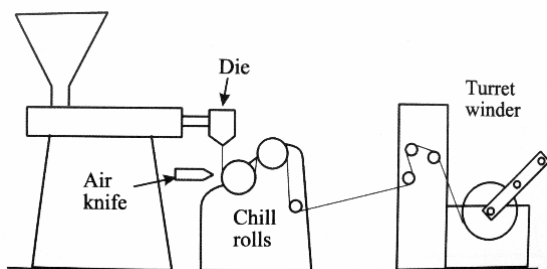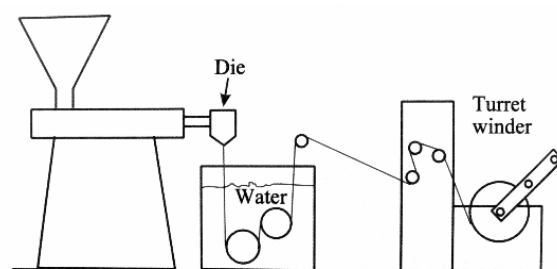

Fig. 2.2 – Cast film line   Fig. 2.3 – Cast quench line

2.1.2 Quench Tank and Water Bath Process

Sometimes the chill roll method does not provide fast enough cooling. In that case, a water-filled quench tank may be used for cooling and solidifying the plastics, as shown in Figure 2.3 After solidification, the film is dried, trimmed, and rolled up. This method used to be widely used for polyethylene and polypropylene, but is now much less common. Since chill roll casting can provide better control over optical properties and thickness [1].

2.1.3 Gauge control

Due to thermal contraction and elastic relaxation, the film or sheet produced by the cold cast process is narrower than the die dimensions, and tends to thicken at the edges, requiring them to be trimmed off. Generated scrap is immediately transported back to the extrusion section and recycled [3]. Any irregularities in the gauge of the film tend to be magnified when it is rolled up. Gauge variations of ±3 % are common in cast film, and this can produce gauge bands in the roll that can cause difficulties in later converting operations. There are two major approaches to minimizing the problem of gauge bands. The oldest method is oscillating the film as it is wound, to produce some randomization of the thickness variations. However this method significantly reduces the width of the web and increases scrap generation. A modern approach uses sensors to monitor the thickness of the web on-line, so that thickness can be measured along both the length and the width dimensions. These values are fed back to the die, permitting automatic computer-controlled adjustments to be made to minimize unevenness in the thickness profile [1], [3].

2.1.4 Orientation

Orientation, stretching the film to produce molecular realignment in the direction of the stretch, is often used to increase crystallinity, barrier properties, and strength in the stretched direction of a cast film, while decreasing strength in the direction perpendicular to the orientation.

If the takeoff speed, the speed at which the plastics is wound up, is significantly higher than the rate of extrusion, the plastics is stretched and uniaxially oriented. Biaxial orientation involves stretching the film in both the machine and cross-machine directions. This can be accomplished in a single step or, more commonly, in two consecutive steps. Both processes are known as tentering. The film is referred to as "balanced if the orientation is equal in the two directions, or "unbalanced if it is more highly oriented in one direction than in the other.

A crystalline polymer must be oriented at a temperature below its melt temperature, but high enough to provide some mobility to the molecules. The higher the orientation temperature, the more the material tends to flow, and the less orientation is produced. On the other hand, if the material is too cold, uneven stretching, with thin spots, and rupture will result. One design guideline is to orient at 60 to 75 % of the range between the glass transition temperature and the melting temperature. After the stretching, or drawing, the film is annealed to improve its thermal stability, if this is desired, and then cooled to freeze the orientation before the tension is released. For successful orientation, the crystallization within the polymer needs to be homogeneous and not excessive [1].

2.2 Blown Film

Blown film extrusion is a continuous process in which the polymer is melted, the melt is forced through an annular die, and the resulting tube is inflated with air into a bubble and cooled. Air is always blown on the outside of the bubble to cool the film, internal bubble cooling can also be used. The film is stretched in the longitudinal and circumferential directions during production, resulting in biaxial orientation of the film. The circumferential stretching is inherent in the blowing process. Longitudinal stretching is imparted by drawing of the film between the extruder and the nip rolls.
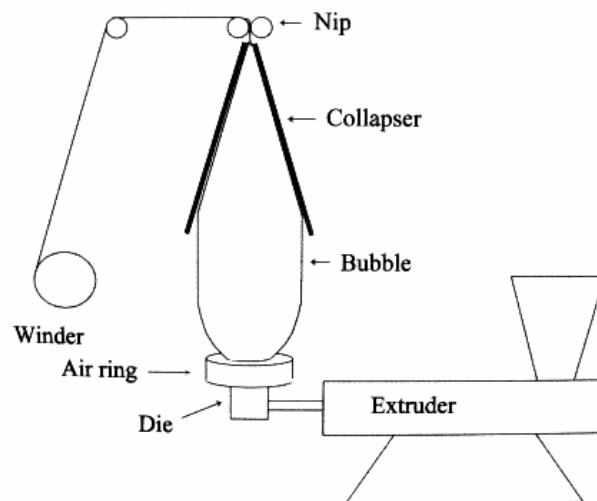
Fig. 2.4 – Production of a blown film

The principal polymers used in blown film production are polyolefins. The major applications are those that require biaxial strength, and include bags of all kinds, as well as agricultural and construction film. In food packaging, coextruded structures with three to five layers, or even more are common [1], [3].

The properties of the film are determined by the blow-up ratio and the linear line speed. The blow-up ratio is the ratio between the diameter of the final tube of film and that of the die. The internal air

pressure that expands the tube into the bubble is typically supplied through a port into the mandrel, the interior part of the die. Once the process is running steadily, little air is usually lost, so make-up requirements are small. When internal bubble cooling is used, air is constantly being exchanged inside the bubble [1].

The travel of the film through the blown film tower is aided by various guiding and sizing devices. When the film is cool enough, the bubble is collapsed by plates and rollers (pinch rollers), and wound up, with or without slitting, gusseting, or other treatment so the blown film process can produce tubular as well as flat film [1], [3].

Blown film tends to be of lower quality than cast film in terms of transparency and uniformity of gauge. The slower cooling of blown film is largely responsible. Slower cooling allows time for a greater degree of crystallinity and larger crystallites to develop, making the film hazier, though producing better barrier properties. The cooling can be more uneven than in the cast process, contributing to greater variation in thickness. It is common to rotate or oscillate the die or nips during extrusion, in order to randomize the thickness variation and produce a uniform roll of film [1].

The collapsed bubble can be fed over a series of heated rollers to reheat it and relieve thermal stresses if a heat-stabilized film is wanted; or it can be heated and reinflated in what is known as the double bubble process, which will be discussed in chapter 2.2.3.

2.2.1 Blown Film Dies

Most dies produced today are spiral channel dies, where the polymer melt is introduced through several ports into spiral channels. It then flows partially up the channel and between the channel and the die wall. This type of smearing flow reduces any existing temperature differences in the melt. As the flow moves up the die channel, the spiral disappears and the melt flows into a relaxation chamber designed to allow the melt to lose the memory of its previous shear history. Beyond the relaxation chamber is the die land itself, which shapes the melt to its final dimensions as it leaves the die [1].

In a coextrusion process, the spiral section and relaxation chamber of the die are replicated for each polymer layer in the final structure. For this reason, coextrusion dies can be very large. Above the relaxation chamber, the melt streams must be combined. If the die is large, there are many layers, or polymers of widely varying viscosities are involved, several combining sections may be used for improved control. Polymers of widely varying viscosities do not flow together in a stable manner, so the channel length must be kept as short as possible in such situations. The polymer with the

lowest viscosity tends to move towards the outer perimeter. Channels designed for tie layers and barrier polymers are generally small because of the small amount of these materials that is needed [1]. It is imperative though to watch polymer's residence time which may not exceed the time to heat the melt above the polymer's heat tolerance.

One important parameter of a die is the drawdown, which refers to the ratio between the speed at which the extrudate is pulled away from the die, and the speed at which the melt emerges from the die. For monolayer films - branched polyolefins can only withstand a drawdown of 16:1 because of the strain hardening of the melt due to chain entanglements; while a linear polymer such as HDPE or LLDPE can be run at a 160:1 drawdown. If the drawdown is too high, the bubble tears off.

In a coextrusion system, the choice of die gap is more complicated because the various polymers are not behaving individually. However, a weighted average of the tensile strengths generally gives a good estimate, and the melt properties are dominated by the characteristics of the heaviest component. The die land refers to the section of the die where the die gap is constant, just before the polymer exits the die. The selection of the length of the die land is determined by the amount of shear orientation that is required. Typical values are a land length to die gap ratio of between 5:1 and 30:1, with a 10:1 ratio the most common.

In addition to the die gap itself, the centering of the die gap is important. Since the polymer is being extruded in an annulus, the centering of the external wall with respect to the internal wall is essential for production of a uniform material.

The most modern die designs include automatically adjustable die lips. A downstream gauging system senses spots in the film that vary from the set-point gauge, and feeds a signal back to an adjustment device on the die lip.

2.2.2 Air Rings and Internal Bubble Cooling

The cooling of the bubble is the next important step in determining the final properties of the film. The original air ring was a pipe with holes drilled in it that wrapped around the bubble. Modern technology has used an understanding of aerodynamics to develop dual lip air rings and internal bubble cooling packages (IBC) that greatly increase production rates and uniformity of the film.

The dual lip concept – There are two air channels outside of the bubble. The first one is designed to lock in the correct bubble shape and to give the bubble stability in the first few diameters above the die; the second one produces the main cooling of the outer surface of the bubble.

For any size bubble, the use of IBC can increase maximum line output. The latest IBC packages also utilize aerodynamic design for the application and extraction of air within the bubble. Automated controls for bubble cooling are now available, and assist in obtaining accurate bubble dimensions. The use of a sizing cage or an ultrasonic gauging ring to control the exhaust air volume flow and maintain the bubble size is now common.

The extrusion of HMW-HDPE has resulted in the development of new specialized cooling technology to produce oriented films. Because of the linearity of the polymer, it has a pronounced tendency to relax and destroy orientation if temperatures are too high. Therefore, HMW-HDPE bubbles are run with a long stalk (neck) before the bubble is forced to stretch in the circumferential direction. This allows the melt temperature to drop sufficiently to maintain the cross-direction orientation and an additional bubble stabilizing iris is used. These films are often used with very thin gauges, 12.5 μm or less [1].

2.2.3   Double-Bubble Process

The double-bubble process involves the extrusion and blowing of a tube of molten plastics in a downward direction. The tube is then cooled, most often using a water bath, reheated to just below the melt temperature, and reinflated. The reinflation along with the increase in haul-off speed provides biaxial orientation. Typically the next step is annealing to relieve thermal stresses and stabilize the film. The double-bubble process is most often applied to PP film, but is also used with multilayer PP or PE-based films. One of the major advantages is that this process can deliver a high-clarity film with precise shrink characteristics and very uniform flatness. The flatness, in particular, is critical for high quality printing systems. The ability to produce uniform shrinkage in both directions is an important property for shrink wrap applications, particularly for printed shrink materials, including labels.

A German company, Kuhne GmbH, has introduced a triple-bubble process, which uses infrared heat, rod heaters, and other annealing techniques in a thermofixation station to impart precise shrink rates to coextruded film [1].

2.3   Film and Sheet Coextrusion

Multilayer structures are often used in packaging in order to take advantage of the properties of several polymers at once. Multilayer structures are made by laminations, coatings, and coextrusions (see Chapter 2.4.). Coextrusion can be used to reduce the cost of multilayer plastics film and sheet.

Coextruded packaging materials are multilayer plastics sheet or film constructions produced from more than one plastics resin in a single step, using either the cast or blown film process. In coextrusion, the materials never exist as separate webs.

Each type of resin is melted in an individual extruder, and the melts are carefully brought together prior to or in the die, in a manner that keeps them in homogeneous layers, without mixing. The process used to combine the polymers is usually different in the cast and blown film processes. In cast processes, as illustrated in Figure 2.5, the polymers are typically combined in an adaptor, called a feed block, before they enter the coat hanger die. This permits a simpler design for the die itself. Multi-manifold dies are used when plastics with widely different flow properties are to be combined, as such systems provide a shorter multilayer flow path before solidification, and thus minimize distortion of the interface.
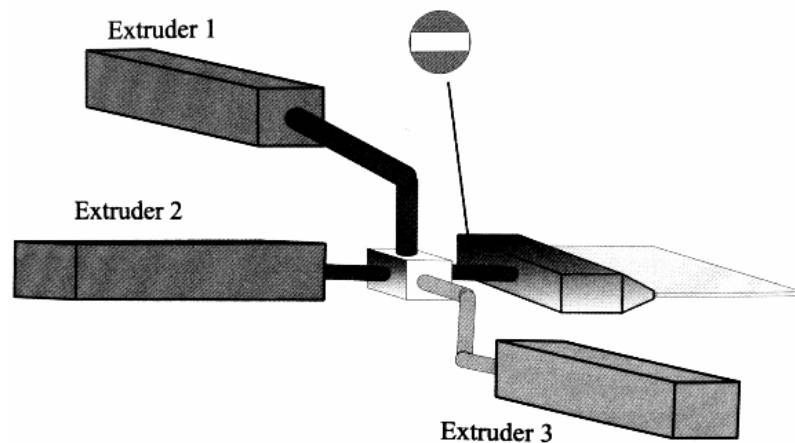

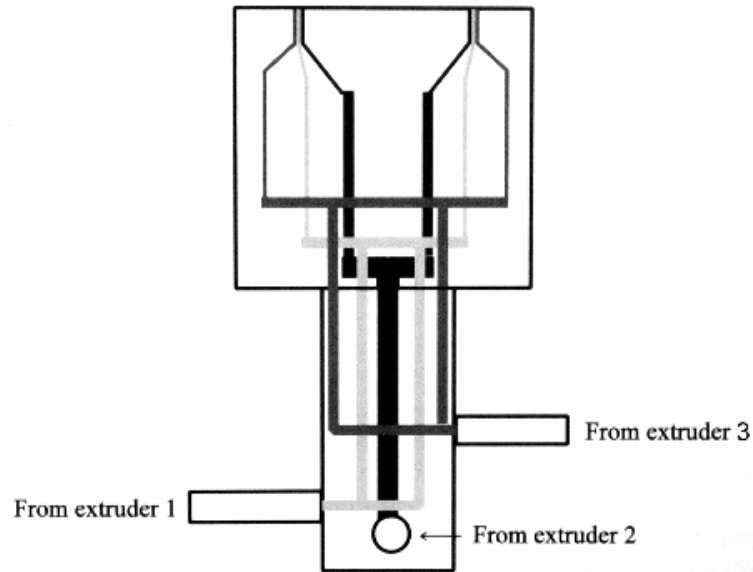Fig. 2.5 – Cast film coextruders and die

Fig. 2.6 – Multichannel blown film die

For blown film operations, a multilayer die is most often used, with cavities, including manifolds, for each polymer cut within the die. The reason for this is that the spiral channel design normally used in the die cannot accommodate pre-combined flows and result in a layered structure. Figure 2.6 shows a schematic of a multichannel die. In such systems, the layers are combined just before they exit the die, or immediately after they exit.
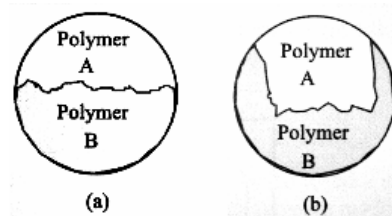
Fig. 2.7 – Viscous instability

Processing of a coextruded material downstream of the die is identical to that of single layer materials. However, in design of the coextrusion, careful attention to the rheology of the polymers, especially flow patterns, melt viscosity, and elasticity, is required in order to prevent layers from intermingling or moving to a position in the structure where they are not supposed to be. Figure 2.7 illustrates some of the difficulties encountered during the flow of multiple materials in a pipe. If two polymers are flowing in a tube, as in Figure 2.7(a), the stability of the interface is dependent on the viscosity differences of the two materials. In order to minimize the energy required for flow, the lower viscosity material will try to cover as much of the wall area as possible, as shown in Figure 2.7(b). A viscosity mismatch of < 3 is necessary for stability in piping and in dies for cast coextru-

sions. Since viscosity of a polymer is dependent on temperature and flow rate, these must be taken into account. The layer thickness affects the shear rate to which the polymer is exposed. As a layer gets very thin, the stress on the melt increases, and may exceed its elongational strength, resulting in discontinuities in the layer.

For many combinations of materials, adhesion between the two desired polymers is weak, and the layers tend to separate under stress. An example is HDPE and nylon, which will not bond to one another. In such cases, it is necessary to add a third component, known as a tie layer, which functions as a thermoplastic adhesive, bonding strongly with both components and providing integrity to the multilayer material. Tie layers must be melted in a separate extruder and fed into the die as an additional distinct layer. Thus, many coextruded materials are three-layer structures, one layer for each of the desired plastics, and an additional tie layer. Structures with four layers or more are also common. For example, structures containing EVOH as an oxygen barrier layer generally require it to be sandwiched between other polymers to protect it from moisture. With the addition of tie layers, this results in a five-layer structure. Each resin in the structure requires a separate extruder, although the melted resin from a single extruder may be split into two or more layers in the coextruded product. [1].

2.4   Converting, Lamination and Coating

Lamination and coating are operations resulting in the production of multilayer flexible structures. The multilayer structures are actually composite materials, which may contain plastics, paper, and/or metal (usually aluminum foil), held together by adhesives. Operators fabricating these flexible structures, called converters, also typically incorporate a printing process. The group of converters makes up the converting industry, which is economically important. The operations, through which polyolefins are mostly used, will be described.

2.4.1   Extrusion Coating and Laminating

Extrusion coating and extrusion laminating operations are normally described together because the process equipment for accomplishing them is essentially the same. Extrusion coating is the operation by which a coating of a thermoplastic material is applied to a substrate web, such as paper. In extrusion lamination, a second web is incorporated and both webs are combined by the adhesive action of the extruded thermoplastic material. The processes are depicted in Figure 2.8. In operations for converting packaging materials, these two processes are often combined in the same line to create a web such as: paper/acid copolymer/film/heat sealant layer.

In the first operation, the paper and the film are extrusion laminated using an acid copolymer as the adhesive. Next, the sealant layer is applied as an extrusion coating. The operation can be accomplished in two passes, or in a single pass in a tandem extrusion line as shown in Figure 2.9. In such a line, both extrusion heads are usually capable of coextrusion, as well.
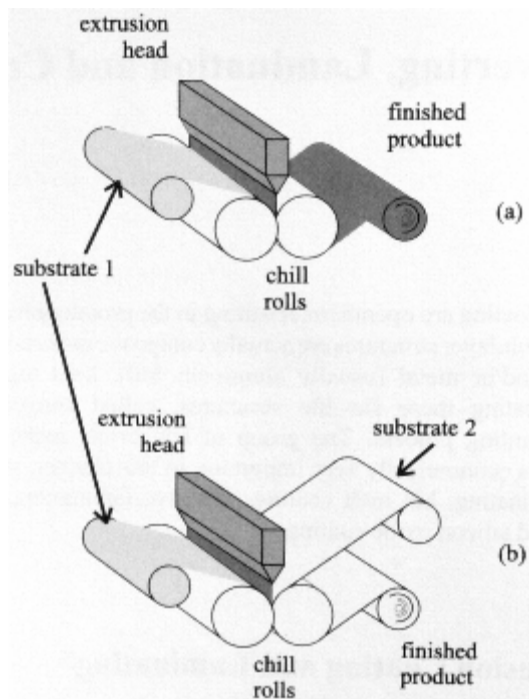
Fig. 2.8 – Extrusion coating (a); Extrusion laminating (b)

Polyethylene coated paper was substituted for waxed paper as a bread overwrap in the 1950s. Since polyethylene is non-polar and paper is polar, there is little or no adhesion between the materials unless the PE can flow into the paper pores, or some modification is done to the PE. A solution to this problem was the discovery that allowing the web of molten PE to drop through the air for a certain distance causes the hot surface to oxidize slightly, creating carboxyl (-COOH) groups on the surface that are polar enough to bond to the paper fibres. To get the PE to oxidize quickly enough for the desired line speeds, the process is often run at a melt temperature of 316 °C or higher. One of the drawbacks to this approach is that the oxidation is not always confined to the surface, but can continue into the bulk of the coating. If too much oxidation occurs, off-odors may develop which can affect the product.

Fig. 2.9 – Tandem extrusion laminating line

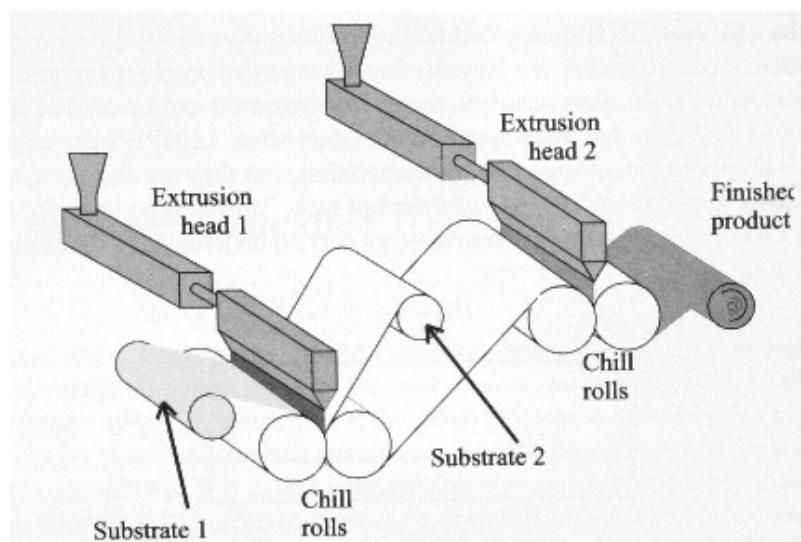To reduce the need for such high temperatures, primers are used to improve adhesion. These primers are organic compounds that are coated onto the paper in-line with the extrusion coating to provide non-polar groups to which the PE can adhere, as well as polar groups which can adhere to the paper. Polyethylene imine (PEI) is one such compound. These primers allow the melt temperature to be reduced to 288 °C.

Primers can be used on film also, but another approach often used with film is to use a polymer that has polar groups on the chain, such as an acid copolymer or an ionomer, for the coating. Polyethylene acrylic acid is a typical acid copolymer. Ionomers are partially neutralized acid copolymers, of which Surlyn™ is the best known. Acid copolymers and ionomers can also be used as sealant layers [1].

Because the polymer melt is expected to drop though an open space before contacting the web, the polymer must have sufficient melt strength to support its weight; also the polymer curtain should not contract too much in the cross-direction (neck-in) during the operation. The distance between the die and the chill roll (the air gap) is typically 152-203 mm in extrusion coating, while in film or sheet extrusion it is much less.

LLDPE's are examples of polymers with poor elongational melt characteristics, but they are desirable as sealant layers in many applications because of their hot tack. They can be used for extrusion coating in a coextruded structure where they are carried on a regular extrusion-coating-grade LDPE layer. The tandem coating line can be used to reduce the cost of producing products that require both laminating and coating, such as a paper/polyethylene/film/sealant type of structure [1].

2.4.2   Hot Melt Lamination or Coating

Hot melt laminating is a close relative of extrusion laminating. This process uses a lower molecular weight adhesive polymer that does not need an extruder to melt and pump it. The material's viscosity in the molten state can be low enough for gravity delivery to the die, but most of the time a pump is used for more accurate control. The process beyond the die is similar to extrusion lamination. The most frequent use of this process is for coating a sealant material on a web. It allows the use of a material with a much lower melting point, which can be advantageous in achieving high production rates [1]. For example EVA copolymers are used as hot melt adhesives.

2.4.3   Adhesive Lamination

The process where a solution or emulsion of a low molecular weight polymer adhesive material is coated onto the surface of one web, before the joining of the second web, is typically called adhesive lamination. If the adhesive layer is dried before the joining of the second web, this is called dry lamination or dry bonding. If the webs are joined while the adhesive is still wet, it is called wet lamination or wet bonding. For wet laminating, one of the webs must be porous to allow the evaporation of the water or solvent from the adhesive layer. A form of wet laminating can be done by using reactive adhesives which dry by cross-linking, and thus give off no volatiles, but this is usually called solventless adhesive lamination.
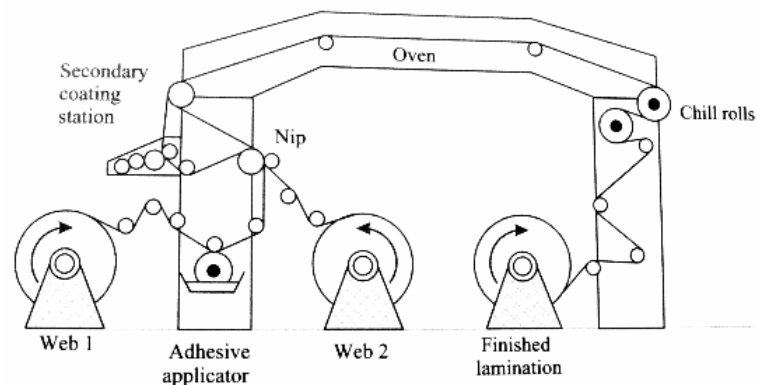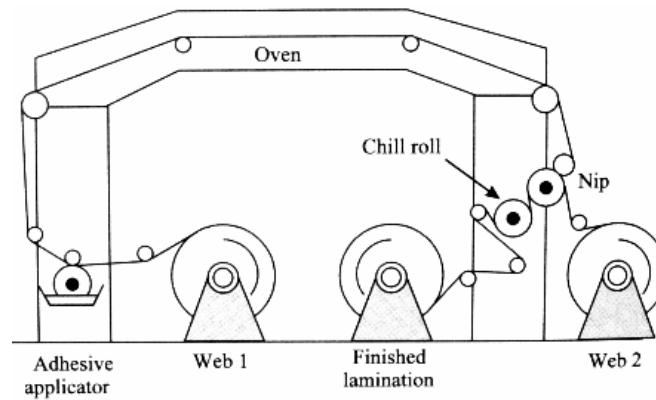

Fig. 2.10 – Wet lamination process

Fig. 2.11 – Dry lamination process

The process equipment for wet or dry laminating is rather similar. In both cases, the adhesive is applied by a roll applicator system. In dry laminating, the oven for drying comes in front of the nip for laminating, and in wet laminating it comes afterwards.
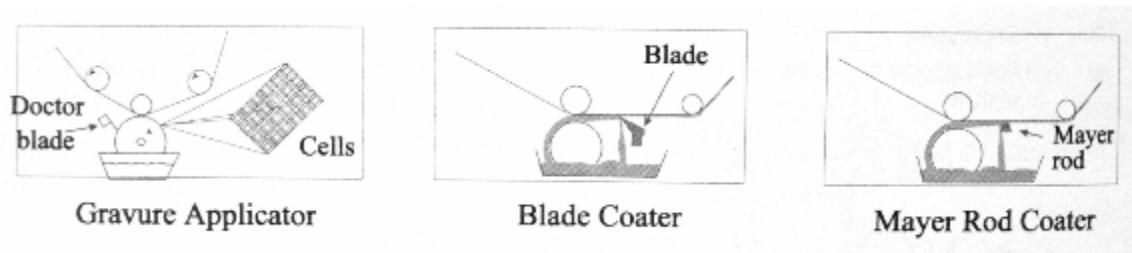
Fig. 2.12 – Various roll-coater setups

As mentioned above, the adhesive is applied to the web by a roll applicator system. These systems require some method of metering the amount of adhesive applied. This can be done by a blade on a gravure roll, a Mayer rod, or a doctor blade, as shown in Figure 2.12. The gravure roll is a metal roll covered with engraved cells. The coating is picked up from the coating pan; the excess is doctored from the roll by a metal blade running in contact with it. A Mayer rod is a stainless steel rod, wrapped with a wire that is rotated while in contact with the web after the adhesive has been applied. The excess adhesive is forced onto the rod, and flows back to the coating pan. A doctor blade is set at a certain distance from the web and removes any excess coating as the web runs by. The gravure roll applicator requires a low coating viscosity; the other systems are less viscosity sensitive. Adhesive lamination can also be done as a part of a printing press operation, if the press is properly equipped. This is the way many OPP/ink/adhesive/OPP/cold seal type structures are made. In this case the laminating station, with its secondary unwind and nip rolls, is inserted in line with the press. An additional printing station following the laminating section applies the cold seal adhesive [1].

2.4.4 Thermal Laminating
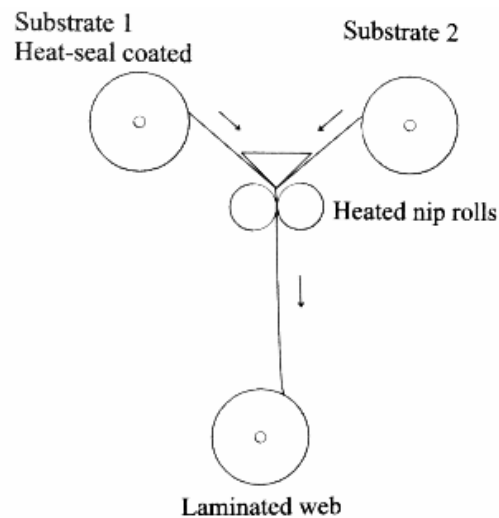
Fig. 2.13 – Thermal laminating

In thermal laminating, heat energy is used to join two substrates together, in a process analogous to heat sealing. One or both of the materials are heated, and then the two substrates are pressed together and cooled, as shown in Figure 2.13. At least one of the layers must contain a plastics on the joining surface that can be heat-sealed to the joining surface of the other substrate. The materials that can be used, then, are similar to those used in extrusion laminating. The main difference is that in thermal laminating, all the layers of the two substrates are already in place; no additional adhesive material is being added during the laminating step [1].

2.5 Thermoforming processing

Thermoforming is a method of forming plastics sheet (or film) into useful packaging by shaping it into or around a mould. It is widely used to produce *blister packages,* in which the product is encapsulated between a moulded plastics blister, usually transparent, and a backing, often paperboard. In production, thermoforming may be highly automated with the various parts of the cycle being sequenced by a computer control system. It is usually considered to be one of the least expensive ways to form three-dimensional packages from plastics. Since most packages or components made by thermoforming are not large, the process lends itself to the formation of large numbers of packages per cycle. The main drawbacks of thermoforming are the inability to form parts to very tight tolerances, and difficulty in making significant undercuts [1].

2.5.1 Temperature Selection

The polymer sheet must be heated to get it to the proper state for forming. The optimum temperature is dependent on the polymer and on the mould design that is being used to make the part. The process parameters depend on the part being manufactured, as well as the starting material.

Amorphous polymers generally have a fairly wider range of forming temperatures that can be used. The forming range generally starts about 20-30 °C above the polymer's glass transition temperature (T_g), with typical forming temperatures 70-100 °C above T_g. Parts must be cooled to 10-20 °C below T_g before they are removed from the mould. For crystalline polymers, the range of forming temperatures is much narrower, confined to within a few degrees of the melt temperature. Special techniques such as solid phase pressure forming (SPPF) can be used to thermoform plastics at temperatures lower than their normal forming temperatures [1].

2.5.2 Forming the Sheet

There are many methods for moulding the sheet of plastics, once it has been softened by heat. The simplest are drape forming, vacuum forming, and pressure forming. Other thermoforming techniques are modifications of these basic methods [1].

Drape Forming - The main forming force is the influence of gravity on the hot plastics sheet, Typically, a positive, or male mould of the part, with a convex shape [1].

Vacuum forming - The main forming force is air pressure, caused by normal atmospheric pressure on one side of the sheet and a near vacuum on the other side. Typically a negative, or female mould, with a concave shape is used. The heated sheet is clamped onto the mould, and vacuum applied, so that the sheet is forced into the shape [1].
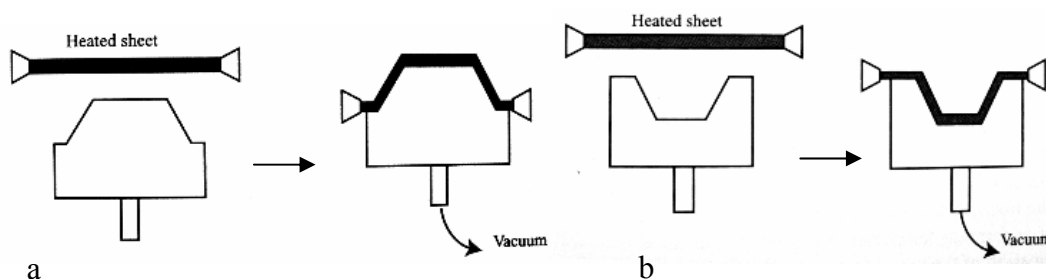

Fig. 2.14 – a) Drape forming; b) Vacuum forming

Pressure Forming – An additional pressure is applied to form the sheet. Either a positive or a negative mould can be used. Most often air pressure greater than one atmosphere is supplied to one side of the sheet, while a vacuum is drawn on the other side. Pressures of 0,14-0,55 MPa are com-

mon, but pressures as high as 3,4 MPa are sometimes used. Pressure forming can achieve better detail and allow more rapid forming than forming methods that have a maximum driving force of one atmosphere [1].
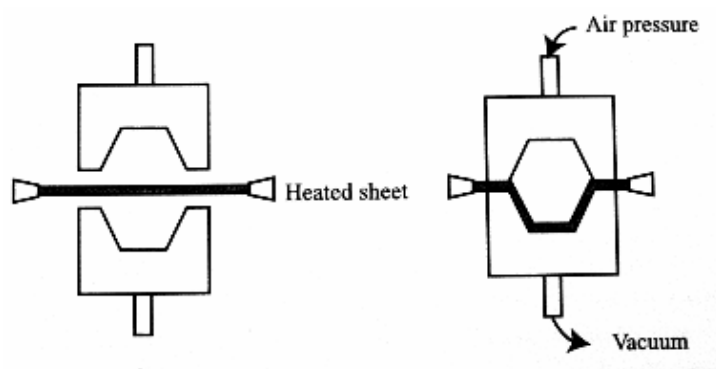
Fig. 2.15 – Pressure forming

In packaging mostly used EVOH copolymers are highly crystalline in nature, and as a result they can be processed only within a very narrow range of temperatures close to the melting point of the polymer. In order to improve the processability, EVOH copolymers with an ethylene content above 38 mol % are habitually used by manufacturers, although the barrier properties to gases and low-molecular-weight organic vapours are lower than those of more preferable EVOH copolymers with lower ethylene content (e.g. 32 mol %).

Appropriate forming processes can be relatively difficult to achieve when combinations of different polymers as in multilayer structures are employed, the reason being that thermoforming is a thermally assisted deformation process whereby the polymer orientates to a different extent depending on the polymer. Several applications in packaging include flexible and rigid containers, where EVOH is coextruded in combination with other polymers like polystyrene (PS) or polypropylene (PP). However, whereas these polymers exhibit optimum thermoforming windows in the temperature range from 110 °C to 150 °C, the EVOH copolymer with 32 mol % ethylene content (EVOH 32) is reported to best thermoform either just above its glass transition temperature (between 90 - 110 °C) or in the vicinity of the melting point (above 160 °C).

2.5.3   Solid phase pressure forming

An alternative can be solid phase pressure forming (SPPF), where the part is formed at temperatures well below the melting point. This process was initially developed to overcome the sagging problem of PP during melt phase thermoforming. Solid phase pressure forming in the region of 110-150°C is nevertheless also difficult to achieve with EVOH 32. It has been observed that EVOH

copolymer results in cracks or fibrillation attributed to a high orientation-induced crystallization rate during the first stages of drawing, especially when deep draws are required.

3   PHYSICAL PROPERTIES OF POLYOLEFIN PACKAGING

There are various very important factors in packaging which must be considered when choosing a packaging material we seek. Not only right barrier propeties, but the material must have sufficient elongation ratio and toughness to prevent damage and loss of it's protectional properties.

In this chapter we wil focus on specific commonly used materials described before and their physical properties, so we could know what to expect. Main properties are stated in tables for better understanding, other, special or interesting facts are described further.

3.1   Summary of physical properties of selected packaging polymers

Table 3.1 - Summary of selected polymer's properties

Polymer Abbrev.	Density		Mechanical properties									
	g/cm^3	lb/in^3	Tensile strength		Elongation at break %	Tensile modulus of elasticity		Ball indentation hardness		Impact strength	Notched impact strength	
			MPa	psi		MPa	kpsi	10-s-value	10-s-value psi	kJ/m^2	kJ/m^2	ft lb/ in of notch
PE-LD	0.914/0.928	0.0329-0.0330	8/23	1140/3270	300/1 000	200/500	28.4/71.1	13/20	1850/2840	no break	no break	-
PE-HD	0.94/0.96	0.0338-0.0345	18/35	2560/4980	100/1 000	700/1 400	99.6/199	40/65	5690/9240	no break	no break	-
EVA	0.92/0.95	0.0331-0.0341	10/20	1420/2840	600/900	7/120	0.99/17.1	-	-	no break	no break	no break
PP	0.90/0.907	0.0324-0.0327	21/37	2990/5260	20/800	11000/1300	156/185	36/70	5120/9960	no break	3/17	0.5/20
PA 6	41275	0.0406	70/85	9960/12090	200/300	1400	199	75	10670	no break	no break	3.0
PA 66	41640	0.0410	77/84	10950/11950	150/300	2000	284	100	14200	no break	15/20	39084

Polymer Abbrev.	Optical properties		Water absorption		Electrical properties						
	Refractive index n_b^{20}	Transparency	mg (4d)	% 24 h	Volume resitivity Ω cm	Surface resistance Ω	Dielectric constant		Dissipation (power) factor tan $_\delta$		
							50 Hz	10^{6}Hz	50 Hz	10^{6}Hz	
PE-LD	1.51	transp.	<0.01	< 0.01	>10^{17}	10^{14}	2.29	2.28	1.5·10^4	0.8·10^4	
PE-HD	1.53	opaque	<0.01	< 0.01	>10^{17}	10^{14}	2.35	2.34	2.4·10"^{4}	2.0·10^4	
EVA	-	transp./opaque	-	0.05/0.13	>10^{15}	10^{13}	2.5/3.2	2.6/3.2	0.003/0.02	0.03/0.05	
PP	1.49	transp./opaque	<0.01	0.01/0.03	>10^{17}	10^{13}	2.27	2.25	<4·10^4	<5·10^4	
PA 6	l.53	transp./opaque	-	1.3/1.9	10^{12}	10^{10}	3.8	3.4	0.01	0.03	
PA 66	1.53	transp./opaque	.	1.5	10^{12}	10^{10}	8.0	4.0	0.14	0.08	

Polymer Abbrev.	Electrical properties					Thermal properties					
	Dielectric strength		Tracking resistance			Service temperature					
						max./short time		max./continuous		min./continuous	
	kV/25 p.m	kV/cm	KA	KB	KC	°C	°F	°C	°F	°C	°F
PE-LD	>700	-	3b	>600	>600	80/90	176/194	60/75	140/167	-50	-58
PE-HD	>700	-	3c	>600	>600	90/120	194/248	70/80	158/176	-50	-58
EVA	-	620/780	-	-	-	65	149	55	131	-60	-76
PP	800	500/650	3c	>600	>600	140	284	100	212	0/-30	32/-22
PA 6	350	400	3b	>600	> 600	140/180	284/356	80/100	176/212	-30	-22
PA 66	400	600	3b	>600	>600	170/200	338/392	80/120	176/248	-30	-22

Polymer Abbrev.	Thermal properties									
	Heat deflection temperature				Coefficient of linear expansion		Thermal conductivity		Specific heat	
	°C		°F							
	VSP (Vicat 5 kg)	1.86/ 045 MPa	VSP (Vicat lb)	264/ 66psi	10^6- K^{-1}	in/in/°F 10^{-6}	W/mK	BTU in/ ft^{2}h °F	kj/kg.K	BTU lb°F
PE-LD	-	35	-	95	250	140	0.32/0.40	2.2/2.8	2.1/2.5	8.8/10.5
PE-HD	60/70	50	140/158	122	200	110	0.38/0.51	2.6/3.5	2.1/2.7	8.8/11.5
EVA	-	34/62	-	93/144	160/200	90/110	0.35	2.4	2.3	9 5
PP	85/100	45/120	185/212	113/248	150	83	0.17/0.22	1.2/1.5	2.0	8.3
PA 6	180	[80/190	[356	176/374	[80	44	0.29	2.0	1.7	7.1
PA 66	200	105/200	392	221/392	80	44	0.23	1.6	1.7	7.1

3.2 Polyethylene

3.2.1 LDPE

Table 3.2 – LDPE properties

Density	0.910 to 0.925 g/cm³	
T_g	-120ºC	
T_m	105-115ºC	
Tensile strength	8.2-31.4 MPa (1,200-4,550 psi)	
Tensile modulus	172-517 MPa (24,900-75,000 psi)	**Stress-Strain Diagram:**
Elongation at break	100-965%	
Tear strength	200-300 g/25 μm	
WVTR	375-500 g μm/m² d at 37.8ºC, 90% RH (0.95-1.3 g mil/100 in² d at 95ºF, 90% RH)	
O_2 permeability, 25ºC	163,000-213,000 cm³ μm/m² d atm (400-540 cm³ mil/100 in² d atm)	
CO_2 permeability, 25ºC	750,000-1,060,000 cm³ μm/m² day atm (1900-2700 cm³ mil/100 in² d atm)	
Water absorption	<0.01%	

LDPE is characterized by its excellent flexibility, good impact strength, fair machinability, good flow properties, low dimensional stability, good oil resistance, fair chemical resistance, good heat sealing characteristics, and low cost. Its transparency is better than HDPE because of its lower percent crystallinity. For the same reason, while it is a good water vapour barrier, it is inferior to HDPE. Similarly, it is an even poorer gas barrier than HDPE. A summary of the properties of LDPE is presented in Table 3.2.

Medium density polyethylene (MDPE), 0.925-0.940 g/cm³, is sometimes listed as a separate category, but usually is regarded as the high-density end of LDPE. It is somewhat stronger, stiffer and less permeable than lower density LDPE. MDPE processes similarly to LDPE, though usually at slightly higher temperatures [1], [2].

3.2.2 HDPE

Table 3.3 – HDPE properties

Density	0.94 to 0.965 g/cm^3
T_g	-120°C
T_m	128-138°C
Tensile strength	17.3-44.8 MPa (2,500-6,500 psi)
Tensile modulus	620-1.089 MPa (89,900-158,000 psi)
Elongation at break	10-1200%
Tear strength	20-60 g/25 μm
WVTR	125 g μm/m^2 d at 37.8°C, 90% RH (0.32 g mil/100 in^2 d at 95°F, 90% RH)
O_2 permeability, 25°C	40,000-73,000 cm^3 μm/m^2 d atm (100-185 cm^3 mil/100 in^2 d atm)
CO_2 permeability, 25°C	200,000-250,000 cm^3 μm/m^2 day atm (500-640 cm^3 mil/100 in^2 d atm)
Water absorption	<0.01%

Stress-Strain Diagram:
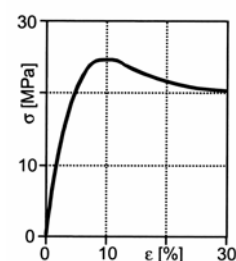
HDPE is characterized by low strength and stiffness, good chemical resistance, ability to be welded, susceptibility to photooxidation (stabilizers). It has milky white colour, smells like paraffin, when burning.

The molecular chains of HDPE homopolymers are long and straight with little branching. HDPE forms a large fraction of ordered, crystalline regions as it cools below its T_m. This close packing produces HDPE with a crystallinity of 65-90 % and contributes to HDPE good moisture-barrier properties and non-transparency. HDPE has excellent resistance to a wide range of chemical compounds: water based products, medium molecular weight aliphatic hydrocarbons, alcohols, acetone, ketones, dilute acids and base. Not acceptable for aromatic hydrocarbons such as benzene. Tensile strength of HDPE can be as high as 45 MPa. Impact strength is primarily controlled by MW although it is affected by MWD. HDPE is also characterized by good moisture barrier properties, and poor oxygen and organic compound barrier characteristics. It has good machinability characteristics. Table 3.3 summarizes HDPE properties.

As is the case for other polymers, the properties are affected by the average molecular weight and molecular weight distribution. As relative molecular mass (or molecular weight) increases, tensile strength, impact strength and resistance to stress cracking increase [1], [2].

3.2.3 LLDPE

The physical properties of LLDPE are controlled by its molecular weight (MW) and density (0.916-0.940 g/cm^3). Due to the increased regularity of the structure and narrower molecular weight distribution, LLDPE tends to have improved mechanical properties, compared to LDPE at the same den-

sity. The greater stiffness results in an increase of 10-15 °C in the melting point of LLDPE compared to LDPE. LLDPE has higher tensile strength, puncture resistance, tear properties and elongation than LDPE. However, LDPE has better clarity and gloss than LLDPE. LDPE also has better heat seal properties [1].

Table 3.4 – Permeability effect on PE density change

Density of polyethylene g/cm^3	WVTR g $\mu m/m^2$ day	Oxygen Permeability cm^3 $\mu m/m^2$ day atm
0.910	0.866	275
0.915	0.779	256
0.920	0.685	225
0.925	0.579	201
0.930	0.465	165
0.935	0.366	137
0.940	0.276	104
0.945	0.244	91.3
0.950	0.208	76.4
0.955	0.185	70.1
0.960	0.145	61.0

3.3 Polypropylene

PP has lower density, higher melting temperature, and higher stiffness (higher modulus) than LDPE and HDPE. These properties determine the applications for PP homopolymer. For example, its higher stiffness and ease of orientation makes PP homopolymer suitable for stretch applications, while its higher heat resistance allows containers made of this material to be sterilizable in an autoclave. The molecular weight of PP typically averages between 200,000 and 600,000. Broad MWD materials are easy to process in injection moulding applications. Compared with PE, isotactic PP is more sensitive to oxidative degradation due to heat and light. Oxidative degradation may produce chain scission that reduces the molecular weight and increases the flow rate. To control this process, antioxidants are added to the resin. Another common additive is an antistatic agent, used to dissipate static charges.

Isotactic PP has extremely good flow properties at a wide range of flow rates, and therefore good processing behaviour. The melt flow index typically ranges from 0.5-50 g/10 min.

The melting temperature T_m is between 160 and 170 °C.

Table 3.5 compares selected properties of oriented and non-oriented PP.

In random copolymers the addition of ethylene, placed randomly in the backbone, prevents the high crystallinity obtained with isotactic PP. Lower crystallinity results in improved clarity and flexibil-

ity, and a lower melting point (152 °C with 7 % ethylene). The density is also slightly lower, 0.89-0.90 g/cm^3. This polymer has better toughness and low temperature impact strength than homopolymer PP.

Oriented PP films (both homopolymer and copolymer) have improved strength, clarity and gloss (brightness) compared to unoriented films [1].

Table 3.5 – Effect of orientation on PP

Property	Non-Oriented PP	Oriented PP
T_g, °C	-10	
T_m, °C	160-175	
WVTR g μm/m^2 day at 90% RH and 38°C	590	240 100-300
Tensile strength, MPa	31-42	50-165
Tensile modulus, MPa	1,140-1,550	High, similar to cellophane
Tear strength, g/25 μm, film	50	Very low CD, very high MD
Heat sealability	Yes, T 177-232°C	No, film distorts
Density, g/cm^3	0.902	0.902
Transparency	Very good	Excellent
Surface adhesivity to inks, etc.	Low	Low
WVTR, g μm/m^2 d at 25°C	100-300	
O_2 permeability, cm^3 μm/m^2 day atm	146,000	98,000 50,000-94,000
CO_2 permeability, cm^3 μm/m^2 day atm		200,000-320,000
Water absorption, %	0.01-0.03	

3.4 EVA

Vinyl acetate is a polar molecule. The inclusion of polar monomers in the main chain during production of branched ethylene copolymers will lower crystallinity, improve flexibility, yield a wider range of heat sealing temperature, and result in better barrier properties, as well as increasing density. These changes in properties result from the interference with crystallinity caused by the presence of random irregularities produced by the relatively bulky side groups from the comonomer, plus an increase in intermolecular forces resulting from the presence of polar groups in the comonomer. The increase in density is attributable to the presence of oxygen atoms with their higher mass, which more than compensates for the decreased crystallinity.

EVA is a random copolymer whose properties depend on the content of vinyl acetate and the molecular weight. As the VA content increases, the crystallinity decreases, but the density increases. Other properties are also affected, resulting in improvement in clarity, better flexibility at low temperature, and an increase in the impact strength. At 50 % VA, EVA is totally amorphous. The increased polarity with increasing VA content results in an increase in adhesion strength and hot tack.

An increase in average molecular weight of the resin increases the viscosity, toughness, heat seal strength, hot tack and flexibility [1].
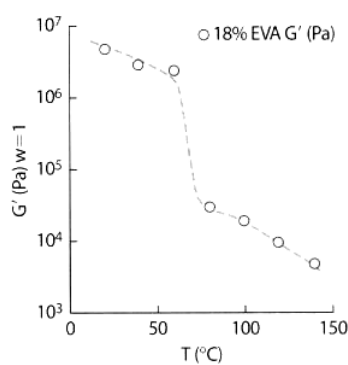

Fig. 3.1 - EVA - dynamic shear modulus vs. temperature

3.5 Ionomers

The ionic bonds produce random crosslink-like ionic bonds between the chains yielding solid-state properties usually associated with very high molecular weight materials. However, ionomers behave as normal thermoplastic materials because the ionic bonds are much more readily disrupted than covalent bonds, allowing processing in conventional equipment. Normal processing temperatures are between 175 and 290 °C. The presence of ionic bonds decreases the ability of the molecules to rearrange into spherulites, thus decreasing crystallinity. The high elongational viscosity caused by the ionic bonds imparts excellent pinhole resistance. Ionomers can resist impacts at temperatures as low as −90 °C (lower than LDPE) [1].

3.6 EVOH

The highly polar OH groups increase the intermolecular forces, while the ethylene groups maintain molecular mobility. Since, as discussed above, the OH group is isomorphous with H, the polymer can achieve a high percent of crystallinity, even though ethylene and vinyl alcohol units are randomly distributed in the chain. The OH groups also make the polymer more compatible with water molecules, so it is much more hydrophilic than PE. The magnitude of all of these effects depends on the percentage of vinyl alcohol. The polymer will have properties similar to PE at a small amount of vinyl alcohol (VOH) content, or will be more like polyvinyl alcohol at a very high VOH content. EVOH properties are summarized in Table 3.6 [1].

Table 3.6 – Selected properties of EVOH copolymers

Property	EVOH 32% Ethylene	EVOH 44% Ethylene
Density, g/cm^3	1.19	1.14
Tensile Strength, MPa	88	68
Tear Strength, N/mm	154	193
T_m, °C	181	164
T_g, °C	70	55
Heat Seal Temperature, °C	179-238	177-238
Oxygen Permeability, cm^3 μm/m^2 day atm		
0% RH	4	2.4
65% RH	13	45
WVTR, g μm/m^2 day at 38°C 90% RH	2500	800

3.7 Physical properties of multilayer systems

Mechanical properties of multilayer systems depends on mechanical properties of layers themselves but also on adhesion of layers where a tie or no-tie procedure can be applied. The lack of compatibility between the polyethylene and the EVOH blends or polyamide (PA) materials allows for easy delamination of the intermediate barrier blend layer. So either additional adhesive layers must be applied during coextrusion process or no-tie PE blends must be used to provide adhesion and prevent undesired delamination of layers. This may, or may not have an impact on properties of the whole system.

To reach desired mechanical or barrier properties it is recommended to prepare a blend of barrier materials. Blends of EVOH are most commonly used because of their good mechanical/barrier properties ratio. For uniaxial tensile behaviour testing of these blends in [4], these blend components were used: EVOH with 32 mol % of ethylene from Nippon Gohsei Co. (Japan), amorphous polyamide (Selar® PA UX-2034), ionomer (Surlyn® AM-7938) The binary (EVOH/ionomer; EVOH/aPA) and ternary (EVOH/ aPA/ionomer) blends prepared were 80/20 and 80/10/10, respectively. Crosshead speed was set to 10 mm/min.

3.7.1 EVOH-based blends

Table 3.7 – Mechanical properties of EVOH based blends commonly in use.

| Sample	V_e (mm/min)	23°C E (MPa)	23°C σ_Y (MPa)	23°C ε_Y (%)	80°C E (MPa)	80°C σ_Y (MPa)	80°C ε_Y (%)	140°C E (MPa)	140°C σ_Y (MPa)	140°C ε_Y (%)
EVOH	10	3381	84	5.6	476	27.2	8.3	71	6.45	17.5
	300	1628	97	5.5	350	32.9	9.3	56	7.93	15.3
	500	489	98	4.1	261	29.4	10.5	53	8.11	14.9
EVOH/aPA	10	3147	75	5.1	447	22.1	7.1	56	5.20	17.7
	300	2535	*	*	400	30.7	8.1	39	5.88	16.5
	500	2054	*	*	322	32.9	8.6	37	6.06	16.4
EVOH/ionomer	10	2617	65	5.8	280	16.7	9.3	51	4.71	16.8
	300	666	73	5.2	234	21.4	9.4	36	5.57	16.4
	500	184	77	⸰	188	21.2	10.0	38	6.15	16.8
EVOH/aPA/ionomer	10	2674	72	5.5	413	21.1	7.7	46	5.46	16.9
	300	953	*	*	341	28.2	8.3	38	6.03	16.8
	500	914	*	*	292	31.1	8.7	35	6.54	16.9

*Sample fails before reaching a yield point.
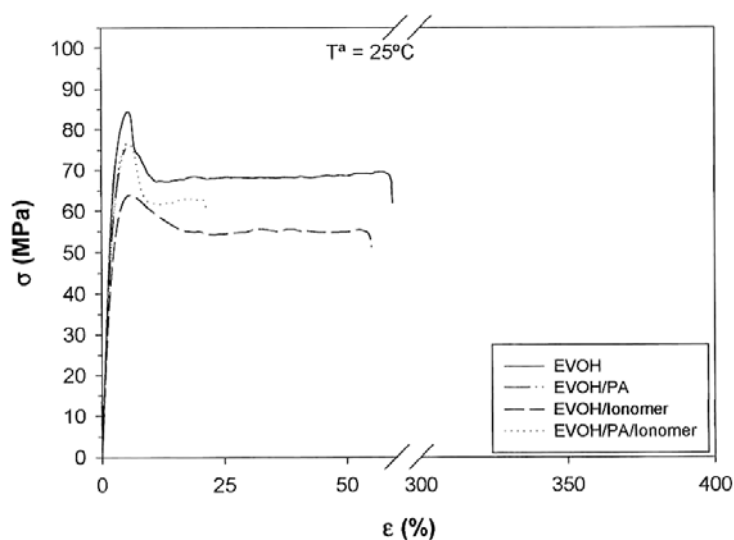
Fig. 3.2 – EVOH blends elongational characteristics at normal temperature.

At room temperature, the EVOH copolymer is below its T_g, and failure takes place for this polymer during extension of the necking transition front over the specimen gauche length, as seen in Figure. 3.2. This uniaxial tensile behaviour of glassy semicrystalline EVOH denotes a poor degree of deformation; this usually depends on the crystallinity level, as well as on the constraints imposed to the amorphous phase by the crystallites during crystallization. In the case of the binary EVOH/ionomer blend and for the same testing temperature (room temperature), the addition of the ionomer promotes an increased flexibility attributed to the rubbery and low crystallinity behaviour exhibited by the ionomer (with melting point at 95°C). This softening is increased during deformation by adiabatic heating when high strain rates are used [5].

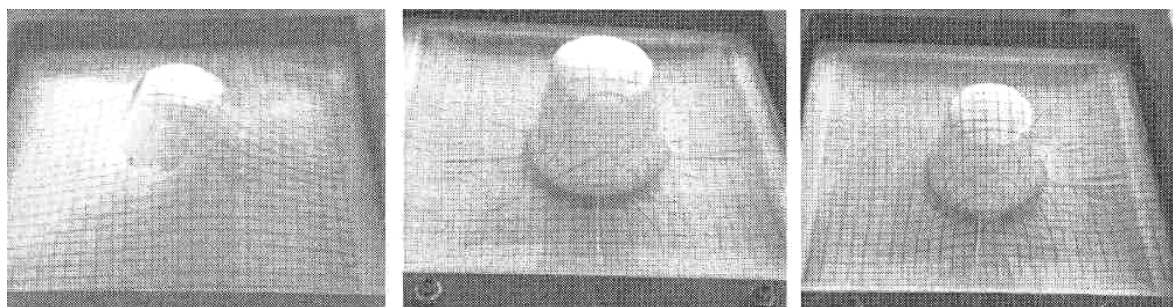Samples of EVOH blends were also subjected to thermoforming.

Fig. 3.3 – Thermoforming (Left-*EVOH*; Middle-*EVOH/PA*; Right-*EVOH/PA/ion*)

Deformation of EVOH is prone to exhibit fissures and microvoids that impede an appropriate thermoforming process in the temperature range 100 -150 °C. It was also found that a binary EVOH/aPA blend did not improve the poor formability of EVOH alone. However, the binary EVOH/ionomer blend exhibited a much wider forming window than EVOH alone in terms of draw ratio and temperature (100-150°C), as a result of the compatibility and flexibilizing effect of by the ionomer. Optimum forming capacity was achieved in a ternary blend at 140 °C by addition of a compatibilized-ionomer to the EVOH/aPA blend.

The hot tensile tests earned out in EVOH sheets showed that the copolymer deforms with certain instability and through a necking process, in accordance to its high crystalline nature. Moreover, such blends may be relatively less sensitive to thermoforming conditions than the other blends in terms of pronounced sag and dimensional stability.

Wall thickness distribution obtained in the thermo-formed parts was significantly affected by the ionomer and amorphous polyamide content. The ternary blend showed a lower reduction of thickness in critical regions, as well as a higher uniformity in the pail, as shown in figure 3.3 [4].
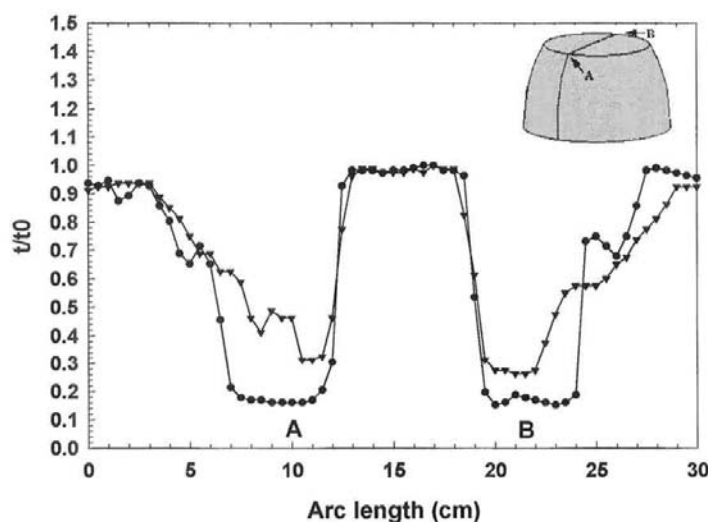
Fig. 3.4 – Wall thickness comparison (triangle - *EVOH/PA/ion*; point - *EVOH/PA*)

3.7.2   No-tie concepts

This covers multilayer structures using PA or EVOH as the central layer and LLDPE/LLDPEgMA blends as external layers without use of any tie layers. Blends of linear low-density polyethylene (LLDPE) and linear low-density polyethylene grafted with maleic anhydride (LLDPE-gMA) were used to promote adhesion between LLDPE and EVOH in a coextruded three layer flat film trying to avoid the use of a tie layer. These particular films could be an option when the equipment for a five-layer system is not available. Using FTIR a continuous decrease of carbonyl absorbance and an increase in absorbance for the ester band was observed when bonding times were increased. For bonding times smaller than 45 sec, a significant decrease in the carbonyl band and an increase in ester band were observed, which suggests the formation of covalent bonding at the interface of the multilayer structure due to the interaction between the anhydride group of the modified polymer and the OH groups of the EVOH copolymer.

Peel strength of the evaluated multilayer films strongly depends on temperature and bonding time, associated with an improvement in chain mobility and an increase in interfacial interactions between polymers. No film delamination was observed when contents higher than 0.08 % of maleic anhydride were used in the blend [5], [6].
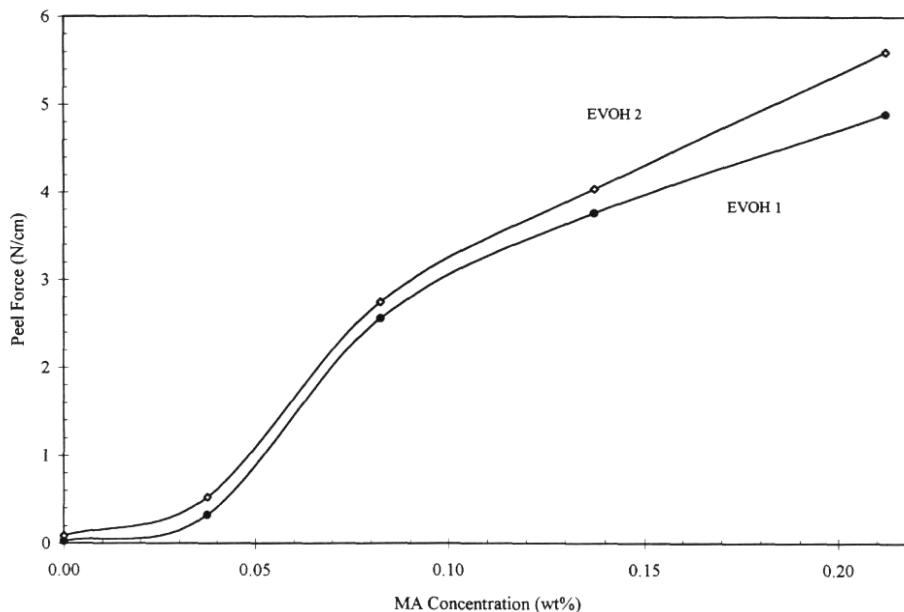
Fig. 3.5 – Peel strength of two types of PE blend / EVOH laminates

Observed changes on the oxygen and water vapour barrier properties of the films were not significant [5], [6].
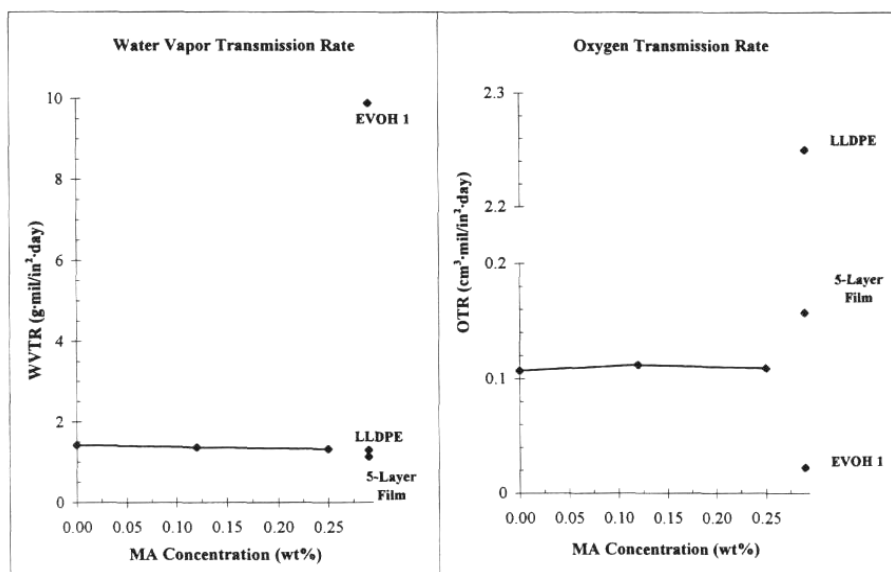

Fig. 3.6 – tie 5-layer and no-tie 3-layer film O_2, H_2O transmission rate.

3.8   Additives

3.8.1   UV Stabilizers

Ultraviolet (UV) radiation from outdoor light and gamma radiation used for sterilization of medical and biomedical products can cause photo-oxidation in polyolefins (especially PP) and other poly-

mers. Highly energetic UV photons can be captured by a polymeric chain, resulting in the breaking of covalent bonds and production of free radicals. Changes of colour, loss of flexibility and gloss, and lower molecular weight are some of the effects that can be produced by photo-oxidation.

One method of protection is to use UV absorbers, agents that absorb the harmful UV radiation and emit harmless radiation of larger wavelength and lower energy, which is dissipated throughout the polymer matrix. An example of this type of stabilizer is hydrobenzophenone, which is commonly used with PE, PP, etc. The Tinuvin™-P family, based on benzotriazoles, is commonly used although it is not as effective in polyolefins as the hydrobenzophenones. One commercial example is Tinuvin™ 326, which is commonly used in concentrations of 0.25-0.30 %. Another example is carbon black, which is an inexpensive material that offers UV protection for PE, and PP, even at low concentrations. UV absorbers can protect package contents, as well as protecting the plastics package itself from UV-induced degradation.

A second group of stabilizers acts by quenching a polymeric chain that has been excited to a higher level of energy by the UV photon, thus bringing it back to a stable state by absorbing the energy in a way that does not promote polymer reactions. An example of this type of stabilizer is organosalts of nickel, which are often used in PP and PE.

Finally, a third mode is when the stabilizer acts as a free radical scavenger, accepting free radicals and preventing them from reacting with the polymer molecules. The highly effective family of hindered amine light stabilizers (HALS) belongs to this group. HALS are antioxidants and provide a regenerative radical trapping process. HALS have permitted new outdoor applications of polyolefins, extending product life and decreasing cost. Tinuvin™ 622 and Tinuvin™ 783 are examples of HALS cleared by the FDA that have low volatility and are effective in carbon black systems and films, respectively. For polypropylene, Tinuvin™ 770 is commonly used.

Combining different stabilizers acting with different mechanisms may trigger a synergistic effect that can provide excellent protection to the polymer. On the other hand, some combinations result in antagonistic interactions that reduce the efficacy of the stabilizers [1].

3.8.2   Antiblocking Agents

Blocking is the tendency of two adjacent layers of a material, such as a polymer film, to stick to each other by simple physical contact. Blocking is particularly a concern for polyolefins. Blocking tends to increase with increasing temperature and pressure. The smoother the surface, the greater is the degree of intimate physical contact, and therefore the greater the blocking. To reduce blocking,

the smoothness of the surfaces may be reduced by incorporating tiny particulates into the polymer. These antiblocking agents produce irregularities on the film surface which reduce contact between the layers of material.

In packaging films, synthetic or natural silicas and minerals are common. Performance is affected by both shape and size of the particles. The preferred average particle size for antiblocking agents in LDPE and PP films is 6-20 % of the film thickness.

Synthetic silicas such as micronized silica gel, fumed silica, and zeolites are often used in high quality packaging films, while naturally occurring silicas and minerals such as clay, diatomaceous earth, talc, and quartz predominate in lower quality materials.

When antiblocking agents are incorporated into PE films, other important properties of the polymer are also affected. These include an increase in stiffness, a decrease in the coefficient of friction, and an increase in haze [1].

3.8.3   Antislip Agents

While blocking is a concern in many applications, at other times, there is a need to increase blocking. For example, a common problem in stacking plastics sacks is a tendency for the sacks to slide off one another. An antislip agent can be used to avoid that problem by increasing friction between the surfaces, or by increasing the attractions between nearby surfaces. Common antislip agents include ethylene/maleic anhydride copolymers, colloidal silica, and finely powdered sand or other minerals. These agents may be compounded into the plastics, or sprayed on surfaces. The particle sizes are generally less than 1 micron, and concentrations of the agents are usually under one percent by weight [1].

3.8.4   Antifogging Agents

Several types of plastics can provide excellent transparency. However, when condensation of water molecules take place on the surface of a package, a thin layer of small droplets of water can be formed. In transparent films and structures, the droplets of water act to scatter the incident light. This phenomenon, called fogging, makes the film or structure appear opaque. The droplets are formed when the polymer surface tension is lower than the surface tension of water, causing the water to remain in droplets rather than forming a continuous layer.

Antifogging additives function by increasing the critical surface tension of the polymer surface, allowing the molecules of water to wet the surface, forming a continuous layer of water which does not scatter light and therefore does not interfere with transparency.

Common antifogging agents are fatty acid esters such as glycerol and sorbitol stearate, fatty alcohols, and ethyloxylates of nonyl phenols. Antifogging agents are incorporated in the resin in levels ranging from 0.5 to 4 %. Factors involved in the selection and use of these additives include polymer type, thickness of the structure or film, performance life, and type of product. If the product is a food, for instance, FDA clearance is necessary for additives. Antifogging compounds can be applied on the surface of the material or compounded internally in the plastics [1].

3.8.5 Nucleating Agents

The use of nucleating agents is also related to obtaining a highly transparent package. The presence of crystallinity is often associated with opacity, as the crystallites scatter light. However, if the crystallites are small enough, they produce much less interference with light transmission than do larger crystallites.

Nucleating agents are often used in highly transparent grades of polypropylene, Adipic acid, benzoic acid, and some metal salts of these acids are often used in polypropylene. For nylon, colloidal silicas are a common choice of nucleating agents. Nucleating agents are not often used with polyethylene [1].

3.8.6 Antistatic Agents

Static electricity can be generated on a polymer surface by friction, such as by rubbing it against another surface. The surface is usually a solid, but may be just air. In packaging, the fast moving film in a continuous converting operation or in a form-fill-seal processing line, for instance, promotes the generation of static electricity on the film. Polyolefins are highly susceptible to accumulation of static charges.

Static can adversely affect a manufacturing operation or process by introducing uncontrolled electrical forces that may result in, for example, materials folding and sticking together. It may also create dangerous conditions such as the formation of sparks leading to vapour explosions. Most polymers are susceptible to the accumulation of electric charges on their surface because of their high resistivity, which prevents the conduction of electrons to dissipate the charge.

Static charges on polymer surfaces can be controlled by the presence of antistatic agents that make the surface more conductive. For example, water within a hydrophilic polymer can act as an antistatic agent and prevent static buildup. The amount of water is important; for example, water in a polyamide in equilibrium with air at 65 % RH acts as an antistatic agent, but at low RH values, water is not effective. Since most polymers used in packaging are not hydrophilic, antistatic additives may be used to control static. Generally, these agents are cationic, anionic, or nonionic surfactants.

For non-polar polyolefins, nonionic antistatics are the most commonly used. These include ethoxylated fatty amines, fatty acid esters, ethanolamides, and polyethylene glycol-esters. The amount used in LDPE is typically around 0.05 %. For packaging of electronics, which can be highly sensitive to damage caused by static charges, considerably higher levels are used, up to 10 % by weight.

Antistats can be applied internally or externally. Internal antistats are compounded into the resin, and act once they migrate to the surface of the polymer. External antistats are applied directly on the surface by spraying, or sometimes by dipping the polymer in a solution of the antistatic. Internal antistatic agents can often provide much longer-term protection than external agents, since additive lost from the surface can be replenished by additional migration of the additive from the bulk. One disadvantage, however, is that antistatic activity does not begin immediately, since time is required to develop a reasonably high surface concentration of the antistat.

An alternative to the use of antistatic additives is the incorporation of electrically conductive fillers or reinforcements into the polymer to make the whole structure conductive. Typical additives that are used for this purpose include aluminum, steel, or carbon powders, and metal-coated glass fibres or carbon fibres [1].

3.8.7 Other Additives

A variety of other additives can be incorporated into polymers, including flame retardants, coupling agents, impact modifiers, and others. It should not be forgotten that, in addition to additives which are deliberately introduced into the resin, plastics may contain substances that are residues of substances produced or introduced at some stage of polymerisation or processing, such as residues of catalysts, solvents, or unreacted monomer or substances which have migrated into the polymer from the contents of the package or from its surroundings [1].

3.9   Yield of Film

The yield of film is a useful parameter in determining how much film, by weight, is required for a given packaging application, where area is the controlling variable. Yield provides a measure of the area of film of a specified thickness that is produced from a given weight of polymer resin. The relationship is as follows:

By definition: Yield = area/weight

In addition, we know: density = weight/volume volume = area * thickness

Therefore, weight = density x volume = density x area x thickness

So **yield** = area/(density x area x thickness) = **l/(density x thickness)**

Thus, yield, Y, can be calculated as the inverse of the density times the film thickness [1].

4 RECENT TRENDS IN POLYOLEFIN PACKAGING

This chapter gives an overview on contemporary approaches in packaging industry. This especially includes stretch and shrink wrap, flexible packaging, special active packaging components, ways to avoid use of tie layer in multilayer concepts and a process of enhancing packaging material by irradiation.

4.1 Stretch and Shrink Wrap

A wrap is the simplest form of plastics package, using a flat piece of plastics film that is folded or wound around the packaged item. Mostly stretch wrap is used for pallet loads of products, serving to unitise and stabilize them during distribution.

4.1.1 Stretch Wrap

Stretch wrap exerts holding power on its contents because the molecules in the film attempt to return to their original conformation after they have been stretched. As long as the elastic limit of the material has not been exceeded, the holding force increases with increasing amounts of stretch, and thus with increasing tension on the film. Because the extent of stretching done during wrapping of products is limited by the potential for product damage and other factors, stretch film is commonly pre-stretched before it is wound on the load. This permits elongations of up to 250 % to be achieved, and minimizes necking-in of the film. Necking-in refers to the tendency of a material width to decrease when it is stretched.

The end of the stretch film is usually secured to the load simply by self-cling. Tackifiers such as polyisobutylene are usually added to the base resin to improve cling. A very smooth outer surface of the film also improves cling. The holding force exerted by stretch wrap decreases over time, especially at elevated temperatures, due to stress relaxation in the plastics.

Most stretch films are LLDPE, modified with various additive packages to provide the desired properties. EVA copolymers and PVC are also used. Coextrusions are often used to provide features such as stronger self-cling on one side than on the other, so that the film sticks to itself as it is wound on the pallet, but does not adhere to adjacent pallet loads [1].

4.1.2 Shrink Wrap

Shrink films, like stretch films, use the tendency of a film to try to return to a smaller dimension after deformation to provide a tight wrap around a packaged object. In shrink film the product is

loosely packaged, and when it is exposed to heat, the film shrinks. The resistance of the product on the film provides the holding force.

To make shrink film, a polymer film can be oriented at an elevated temperature and the orientation frozen by rapid cooling. When the film is subsequently heated, the molecular memory of the polymer causes it to attempt to return to its original dimensions. Lightly cross-linked materials are often used to increase the tendency to shrink. In that case, electron beam irradiation of the plastics film produces free radicals, which then react to produce cross-links between adjacent molecules. The presence of these cross-links means the material will no longer become liquid and flow at its normal melting temperature. That, in turn, allows the shrink film to be exposed to high temperatures, at or above its former melt temperature, without flow, so these elevated temperatures can be used to promote shrinking.

Shrink wrapping starts with loosely sealing the plastics around the product, followed by passing the package through a shrink tunnel, where it is exposed to heat. If the temperature, residence time, and size of the package and product are chosen properly, then a tightly wrapped package comes out of the shrink tunnel. Because exposure to the heat is brief, even products with some temperature sensitivity can be packaged in this way.

Over time, shrink wrap, like stretch wrap, tends to loosen somewhat, due to creep and stress relaxation, with the loss of holding power increasing at higher temperatures.

Shrink wrap materials include PE, PP, and PVC, among others. Some shrink wrap is used for pallet-loads of goods [1].

Fig. 4.1 – Example of shrink wrap use

4.2   Flexible packaging

The major advantage of flexible packaging is economy. Flexible packaging makes very efficient use of both materials and space, so distribution packaging can be smaller. Forming packages is generally rapid and simple.

The primary disadvantages of flexible packaging are its lack of convenience for the user and lack of strength. Flexible packaging has no appreciable ability to support a load, so secondary packaging must provide any strength that is required. Flexible packages tend to be difficult to open, and they are often impossible to reseal effectively.

One feature that is increasingly being used is zipper closures to provide reseal capability. Easy-peel seals have been developed to facilitate opening, and some of these provide for reclosure.

Use of pouches has been growing very rapidly in recent years, as new structures provide improved barrier and retortability, allowing these pouches to substitute for rigid packages such as cans, as well as for paperboard cartons. Flexible packaging, for a number of years, has been the most rapidly growing segment of the packaging industry, accounting for about half of all use of plastics in packaging.

These packages can be categorized as bags, envelopes, sacks, and pouches. All are made by folding and sealing the plastics together in some way [1].

4.2.1   Pouch Styles

Pouches can be made in a variety of styles. However, the majority can be categorized into one of four groups: pillow pouches, three-side seal pouches, four-side seal pouches, and stand-up pouches.

Pillow Pouches are constructed with seams at the back, top, and bottom. They tend to pillow in the middle (potato chip bags). The seam or seams in a pouch can be made in a variety of ways, but the most common is heat sealing. The back seam of a pillow pouch is most often afin seal, where the two inner layers of the material are brought together and sealed, resulting in a seal which protrudes from the back of the finished pouch. Sometimes a lap seal is used, where the inner layer of one side is sealed to the outer layer of the other side, producing a flat seal. The fin seal produces a stronger seal and requires only the inner layer of the material to be heat-sealable. The lap seal uses slightly less material, but is weaker and requires both layers of the pouch to be heat-sealable. The top and bottom seals are made between inner layers of the pouch material, analogous to the fin seal. If de-

sired gussets can be incorporated into the pouch design, permitting the pouch to expand in cross-section to a larger degree.

Three-side seal pouches contain two side seams and a top (or bottom) seam. The remaining side contains a fold. All seals are made between inner layers of the pouch material. If the pouch design incorporates gussets, these pouches can be capable of standing erect.

Four-side seal pouches are made from two webs of material, which are sealed together at the top, bottom, and both sides of the pouch. Unlike the pouches previously discussed, the front and back sides can be made from different materials. These pouches may have a variety of decorative shapes.

Stand-up Pouches -The term stand-up pouch refers to a pouch that is able to support itself in an upright position when it is filled with product. Such pouches contain gussets that expand when the product is added, providing a relatively flat base to the pouch. Design of the gusset, usually a horizontal bottom gusset, is critical in pouch performance. It can be made from a separate piece of material, sealed to the rest of the pouch, or the pouch material can be folded into a W shape to produce the base.

These pouches are now available with snap caps and threaded closures, nozzles, and zippers for resealability. One company has even introduced a low cost hook-and-loop ventilating closure for flexible packaging.

The pouches are printed as rollstock, facilitating the use of high-quality multicolor images. Technological innovations in production of high barrier materials have also been important in ability to use pouches for sensitive products. A significant drawback to the use of pouches is their slow line speeds, which for beverage packaging is often only about half the speed used with bottles of the same capacity [1].

4.2.2   Forming Pouches

The most common way to make pouches (and to package products in pouches) is to use a form-fill-seal (FFS) machine, in which pre-printed roll stock is formed into a package and the package is filled and sealed with product, all in a continuous operation within one piece of equipment. Cutting the pouches apart is usually accomplished within the FFS machine, as well.

An alternative to form-fill-seal equipment is to use preformed pouches. In this case, the preprinted pouch is supplied ready to be filled with product, and then after it is filled the top seal is made. In such cases, filling and sealing are most often done on two separate pieces of equipment.

For large operations using materials which seal readily, form-fill-seal operations are usually the most economical. However, use of preformed pouches requires less capital investment, since the equipment is simpler and less expensive. It also requires less quality control, since only one seal must be monitored. Therefore, for low volume operations or materials that are difficult to seal correctly, use of preformed pouches can be advantageous [1].

4.2.3 Retort pouches

Retort pouches are pouches that are designed to be filled, usually with a food product, and then retorted (heat-sterilized in a procedure analogous to canning) to produce a shelf stable product, one that does not require refrigeration. Their flexibility, smaller volume, and much lighter weight than cans are a significant advantage.

The initial design for retort pouches, and the one still used by the military, was a multilayer lamination containing an outside layer of polyester, a layer of aluminum foil, and an inside layer of polypropylene. The polyester provides strength and puncture resistance, the aluminum provides barrier, and the polypropylene provides the sealant and product contact layer. A significant disadvantage of this structure is that the food cannot be heated within the pouch by microwaving.

Consequently, the retort pouch is not easy to seal. In addition to the difficulty in working with polypropylene as the sealant layer, to ensure sterility, any wrinkling in the seal area must be eliminated.

Because of their thin profile and high ratio of surface area to volume, food products can be sterilized in less time, typically 30 to 50 % less than is required for canning.

A variety of complex ultra-high barrier laminate structures are now available as alternatives to the old aluminum foil structures [1].

4.2.4 Bulk bags and heavy-duty bags

Bulk bags and heavy-duty bags are designed for packaging large quantities of solid or liquid product. They can contain as much as 5,000 kg and, therefore, must have high tensile strength. Woven PP fabric is usually the material of choice, although HDPE, PVC, and polyester fabric are also used. Some bags, especially in smaller sizes, are made of film, usually LLDPE or HDPE, rather than fabric. Other bags include a plastics film layer in a construction that is mostly paper. An alternative is to use the plastics as a coating on the paper. HDPE, LDPE, PVDC, PP, and combinations are all used in such applications.

Bags made of woven fabric do not generally provide sufficient containment for liquid products, so such bags often incorporate a film liner. Polyethylene is used most often, but aluminum foil or PVDC copolymers can be used to provide improved barrier ability. The liner may be a single or multilayer construction.

Large bulk bags are most often designed to be filled from the top and emptied from the bottom. Filling and discharge openings may be sealed, or may simply be tied shut. Spouts or other dispensing devices may be included, or the bags may simply be cut to open. Handling devices, such as loops of fabric, are often incorporated. Ultraviolet light stabilizer must be incorporated into the resin formulation if the bags will be stored and used outdoors [1].

4.3   Enhanced packaging shrink film and shrink tubing

A major application that has achieved commercial success is bioriented shrink film for packaging. An electron-beam crosslinked bioriented polyethylene has been presented. Crosslinked film dominates this market because of a number of advantages over the non-crosslinked competitive polyvinyl chloride and polypropylene films. Polyethylene typically has better tear resistance and higher total shrink than these materials. This yields machinability advantages on automated shrink-wrap machines, greater abuse resistance and improved appearance on a finished package. However, bioriented polyethylene must be sealed and shrunk in a narrow temperature range to prevent shrink-induced "burn through". Electron-beam crosslinking increases the high temperature strength and abrasion resistance of bioriented polyethylene. The result is a film with broad heat-seal and shrink temperature ranges combined with the other advantages of bioriented polyethylene.

Another similar, highly successful, commercial electron beam crosslink application is shrink tubing, which is used extensively for electrical connections and medical devices.

4.4   Avoiding the use of tie layer in multilayer films

Because of the incompatibility across the whole range of compositions, an intermediate tie layer to promote adhesion is needed, thus forming a PE/tie/EVOH/tie/PE five-layer film.

Blends of linear low-density polyethylene (LLDPE) and linear low-density polyethylene grafted with (LLDPE-gMA) can be used to promote adhesion between LLDPE and ethylene-vinyl alcohol copolymer (EVOH) in a coextruded three layer flat film, trying to avoid the use of a tie layer. These particular films could be an option when the equipment for a five-layer system is not available. An

increased T-peel (layer-layer) strength observed when using maleic anhydride contents higher than 0.08 %. It suggests a good interfacial adhesion between layers.

(1)
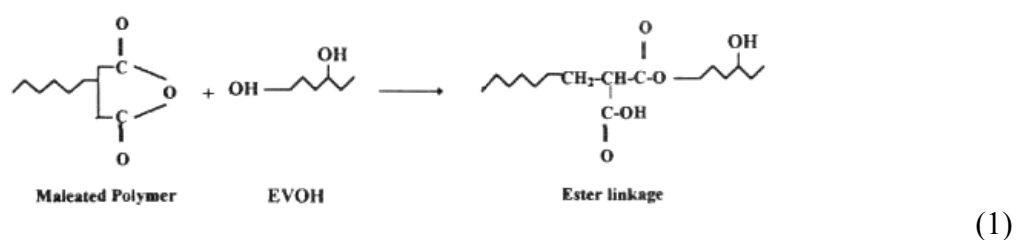
This increase could be associated with specific interactions between the LLDPE-gMA and the EVOH, as the development of covalent bonds through the reaction of the anhydride with the EVOH hydroxyl groups across the interface. This was proved by the FTIR analysis that showed an increase in the ester band absorbance with an increase on the maleated polymer content and bonding time indicating that a chemical reaction occurred, at the interface. The observed changes on the oxygen and water vapour barrier properties of the films were not significant.

4.5   EVA copolymers as tie layers

A new line of EVA copolymers designed for use as adhesive tie layers is said to offer advantages over conventional EVAs in specialized coextrusion applications such as food and beverage packaging. Levamelt copolymers from Lanxess Corp., Pittsburgh, contain 40 to 80 % vinyl acetate, compared with less than 40 % VA levels in typical EVA copolymers used as adhesive tie layers. Such high VA content is said to improve both processability and the quality of multilayer film packaging. These EVAs can be used in cast or blown films and comply with safety FDA regulations for adhesives, polymeric coatings, and closures with sealing gaskets [7].

4.6   Radiation crosslinking

Application of radiation doses in the 50-200 kGy range can create crosslinking between reaction sites to form separate polymer chains. The resulting polymer retains many of the physical properties of the original polymer such as modulus, melting point and glass transition. One major exception is that with sufficient radiation exposure, the polymer becomes a crosslinked network and highly resistant to flow at high temperatures.

For example EVA copolymer with approximately 18 % vinyl acetate content. At the standard steam autoclave temperature of 121 °C the polymer can not maintain its shape, because it is above its melting point. However, on exposure to approximately 100 kGy of accelerated electron-beam (beta)

radiation, physical properties change and previously shaped articles can maintain their shape and become autoclavable.

For example, for the EVA polymer, a significant amount of acetic acid is produced as a by-product of radiation processing. Polymer systems other than EVA, the radiolysis by-products can be reduced to acceptable levels[8].
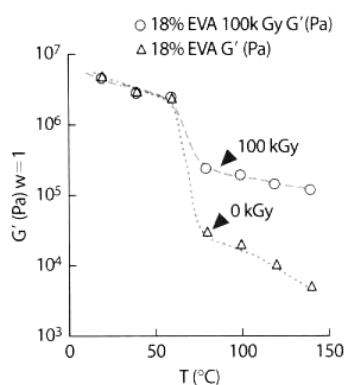

Fig. 4.2 – Radiation crosslinking effect

4.7 Spoilage scavenger systems

Spoilage scavenger systems consisting of films impregnated with chemically reactive additives are also being developed for ethylene and other compounds which affect spoilage of products. E-I-A Warenhandels GmbH of Vienna, Austria, offers a master batch additive system which absorbs ethylene, as well as other undesirable compounds that can form inside packaged fruits, vegetables, and flowers, such as ethanol, ethyl acetate, ammonia, and hydrogen sulfide [1]. These scavengers are part of active packaging further discussed in chapter 5.

4.8 Fragrance enhancers

Fragrance enhancers, as their name indicates, are used either to eliminate undesirable odours or to produce desirable ones. Besides trash bags, special food packages or blow-moulded bottles may also contain additives that prevent the product from picking up undesired odours from the surroundings, or that provide for generation of desired odours. Since odours and flavours are highly associated, these same additives can affect taste as well as smell [1].

DuPont has developed at least two means of removing odours, one originally intended to remove polyolefinic extrusion odours. Molecular sieves are capable of physically removing unwanted odours. Another approach has been to blend organic reactants such as polyethylene imine with the

polymer to deliberately scavenge the internal package odours [9]. These scavengers are also part of active packaging further discussed in chapter 5.

4.9 Intellipack

Landec Corporation's Intellipac materials can be engineered to change gas or water vapour permeability with changes in temperature. These materials are capable of controlling the passage of gases from the external air into the package or from the interior to the air, and to thus control the ratio of oxygen to carbon dioxide in modified atmosphere packages. These package materials and structures have the potential to precisely control the gas mixture with the package through distribution [9].

4.10 Special purpose multilayer bottles

Ampac Flexibles, has launched PureFlex, a stand-up pouch structure for water and other taste and odour-sensitive beverages. Traditionally water has been one of the most challenging beverages to package because of its odourless and tasteless qualities. Ampac's PureFlex is a seven to nine layer proprietary coextrusion featuring an organoleptic sealant layer, nylon and ethylene vinyl alcohol (EVOH) copolymer layer for additional oxygen barrier. The nylon is said to help provide structural strength while acting as a barrier against odour ingress. Suitable applications for the PureFlex stand-up pouch include specialty waters, nutraceuticals and sports endurance drinks. The EVOH layer widens the applications to include juices, wines and other beverages requiring added oxygen barrier to achieve shelf-life requirements [10].

4.11 Improving decorative film technologies

CTT film which utilizes Cold Total Transfer technology for film-based packaging decoration. This technology can apply holographic or silver images to a package without the risk of memory issues for higher-quality aesthetics. In addition, print-ready CTT Film eliminates the costly intermediary steps necessary when utilizing heat-transfer methods and can also be sold directly to printers. This new film technology does not transfer film during the image-transfer process, which results in a lighter package weight and reduced shipping costs.

Combining this technology with hologram design capabilities allows brand owners to incorporate brand protection features into packaging.

4.12 New Metalocene polyolefins

AtoFina Petrochemicals in Houston has shown metallocene medium-density polyethylene (mMDPE) film and blow moulding grades, as well as a family of metallocene PP (mPP) homopolymers and copolymers for film and injection moulding. Based on the company's own catalyst technology, these Finacene resins boast improved mechanical, optical, and barrier properties, as well as excellent processability.

PE for clear, stiff film

First mMDPE is Finacene M 3410 EP for blown film. Compared with other mPE resins, it reportedly brings a unique combination of excellent processability, good compatibility with LDPE and LLDPE, high stiffness, and excellent optical properties (9 % haze and 60 gloss rating at 45°).

In 25μm film produced on an LLDPE extrusion line, M 3410 EP has 35 % higher slow-puncture strength and 60 % higher tear strength than conventional MDPE. Applications include tissue and towel overwrap and high-clarity shrink film.

The new material has also found use as a 20-30 % blend component for downgauging LDPE monolayer films. A 70/30 blend of LDPE and M 3410 EP at 27μm gauge compares favourably with 35μm of a liner-grade LDPE. The thinner film has higher stiffness and tensile strength, reduced blocking, and good optics.

Finacene M 3410 EP can also be used as a substitute for LDPE to add bubble stability to LLDPE-rich monolayer films. M 3410 EP provides all the processing benefits afforded by LDPE but with much less deterioration of LLDPE mechanical properties. An 80/20 blend of 25μm. LDPE and M 3410 EP yields less gauge variation than an 80/20 LLDPE/LDPE blend at equivalent output rate. What's more, the M 3410 EP blend has better tear strength, higher stiffness and tensile strength, enhanced slow puncture strength, and less blocking.

A 70/30 blend of LDPE and M 3410 EP can be used to downgauge clarity shrink film while increasing shrink-retention force by 20 % compared with a traditional 70/30 LDPE/LLDPE mix. Such a blend also offers enhanced stiffness and tensile strength, higher tear strength, and better creep resistance. Adding M 3410 EP to LDPE shrink film also prevents burn-through in the shrink tunnel. In coextruded structures, blending M 3410 EP into the core layer produces a high-clarity film with good stiffness for downgauging.

M 3410 E is also being used as a majority component (up to 90 %) to downgauge tissue and towel overwrap. It offers increased stiffness and tensile strength, excellent bubble stability, low gels, high

gloss, and good contact clarity. Stiffness and MD tear strength can be tailored for specific applications by blending with Finathene 6410, a 0.961-g/cm^3, medium-molecular-weight, high-clarity homopolymer HDPE.

In coextruded film for flexible specialty packaging, M 3410 E provides excellent clarity, low seal-initiation temperature, and good seal strength, stiffness, tensile strength, and toughness.

MDPE for glossy bottles

Finacene BM359 SG, the new mMDPE extrusion blow moulding grade, is touted for its exceptional gloss, flexibility (for squeeze bottles), and processability (high output without melt fracture). Its gloss outshines that of previous glossy HDPE resins by 50 to 100 %. In fact, this hexene copolymer boasts surface gloss comparable to glossy PP (60 to 90 gloss rating at 50°) and is suited to packaging of personal-care products like shampoos, sun creams, body lotions, and cosmetics. BM350 SG is reportedly also glossier than other MDPEs and does not need any blending to obtain the right squeezability. BM359 SG offers excellent processability in monolayer uses for flexible high-gloss bottles and in coextrusions with an inner layer of stiffer HDPE. BM359 SG also sports high ESCR(>1000 hr).

mPP for film & molding

AtoFina now offers a family of isotactic mPP homopolymers and random copolymers for cast film, heat-seal layers, and injection moulding. Homopolymers range in MFR from 3 to 40 g/10 min and melting point from 150 to 156 °C. Random copolymers range from 7 to 30 MFR and 114 to 147 °C melting point.

For cast film, AtoFina offers mPP homopolymers and copolymers with excellent clarity and moisture barrier. They are aimed at higher-end food and non-food packaging. The material possesses improved processability and higher line speeds due to reduced draw resonance compared with other PP homopolymers and random copolymers.

The Table 4.1 shows that Finacene mPPs have comparable or better tensile strength relative to non-metallocene PPs, plus improved stiffness, clarity, and vapour transition rate.

Table 4.1 – Properties of Finacene mPP vs. conventional PP and Random copolymers.

Resin Type	Tensile Str., MPa	Secant Mod., MPa	Haze,%	MVTR mg/m^2 /24 hr	Melting Point.°C
Homo-PP	48.2	482.6	5	45	163
Homo-mPP	53.7	655	1	32.2	150
2% RCO	48.2	448	1.7	45	148
2% RCO mPP	42.7	551.5	0.5	25.8	137
4% RCO	46.7	372.3	2.2	58	134
4% RCO mPP	48.2	503.3	0.4	38.7	131

For sealant layers, the company particularly recommends its higher-ethylene-content mPP random copolymers. They can be used in clear and opaque multi-layer BOPP films for snack-food packaging. Finacene materials have much lower extractables, seal-initiation temperatures as low as 100°C and excellent hot tack.

For injection moulding, AtoFina offers clear homopolymers and random copolymers. They have scored commercial success in containers and housings for office equipment.

Applications involve replacing standard PP and other clear polymers like PS, acrylonitrile-butadiene-styrene copolymer (ABS), and acrylics. [11]**.**

5 CONVENTIONAL APPROACHES TO IMPROVEMENT OF BARRIER PROPERTIES

Several ways to improve certain barrier characteristics can be employed. Either the addition of an additional layer(s) during coextrusion/extrusion/lamination process or the use of a customized polymer blend or the use of additional systems (active packaging) should be profitable to improve barrier characteristics of a package. But an indispensable role in product shelf-time takes the environment in which is the package processed and stored. Product storage or handling in bad conditions significantly reduces lifetime of product and increases chance of package breach and destruction of its contents.

5.1 Active packaging

Active packaging means that the packaging material itself contributes on its content protection by modifying internal conditions. Common method is the use of substances which reduce levels of oxygen, moisture or microbial threat inside of the package.

5.1.1 Oxygen Scavengers and Desiccants

Oxygen scavengers in a package can help protect the product from oxidation. This is a relatively new area, with few applications at present, but a large potential. The first oxygen absorbers used in packaging were just sachets of iron oxide which were placed inside the package. Some packaging systems have used pressure-sensitive labels, applied inside the package, which contain an oxygen scavenger.
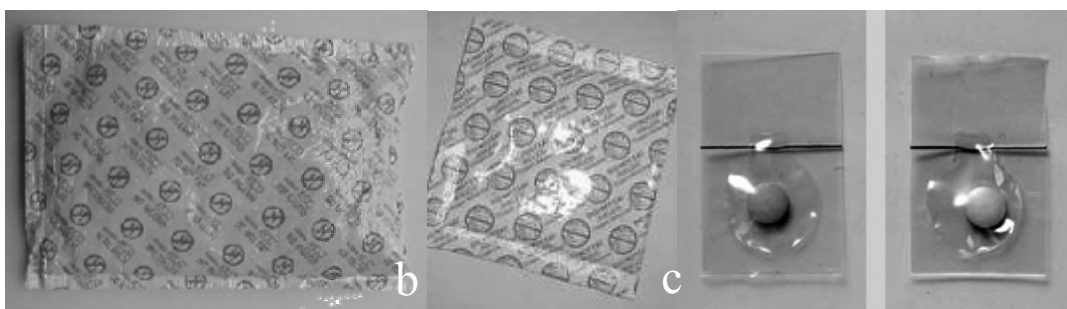

Fig. 5.1 – Oxygen scavenger sachets

Figure 5.1 shows some examples of Oxygen scavenger sachets presently used. Figure 5.1a shows ATCO FTM 2000 S, sulphur free, approx. 120 x 80 x 15 mm. One sachet scavenges 10 l of air. Fig-

ure 5.1b presents Ageless 300 ZP300E, approx.. 60 x 60 mm for 1.5 l of air and Figure 5.1c shows indicator tablets turning pink below 0.1 % oxygen and returning to blue above 0.5 % oxygen.

For a variety of reasons, including simplifying packaging line operations and avoiding the risk of consumers inadvertently consuming the scavenger along with the product, there is a desire to replace these systems with packages with built-in oxygen scavengers. Most of the newer systems are designed to be added to the packaging resin in the form of master batches, and be dispersed throughout the material. For oxygen, the additives generally consist of an oxidizable component, often a metal, oxidation promoters, and sometimes fillers [1].

In general, O_2 scavenging technologies are based on one of the following concepts: iron powder oxidation, ascorbic acid oxidation, catechol oxidation, photosensitive dye oxidation, enzymatic oxidation (e.g. glucose oxidase and alcohol oxidase), unsaturated fatty acids (e.g. oleic acid or linolenic acid) or immobilized yeast on a solid material[4].

Metal-free absorbents commonly use mixtures of organic compounds such as phenolics, glycols, and quinones. In some cases, oxygen-absorbing monomers can be incorporated into the polymer structure during polymerization, to make an inherently oxygen-absorbing plastics. Most of the additive systems are activated by moisture.

Cryovac markets an oxygen scavenger film for modified atmosphere packaging, which has a proprietary polymer coextruded as an invisible layer of the final structure. The scavenging activity is activated just prior to sealing by a Cryovac ultraviolet light triggering unit which is installed on the processor's packaging line. The activity then continues without requiring further light exposure, until the capacity of the film is exhausted. The system reportedly can reduce residual oxygen levels from the normal 0.5-1 % range down to parts per million in 4-10 days. The polymer can also be used in lidstock for thermoformed packages [1].

If the meat is packed along with oxygen scavengers it shoud be considered that oxygen has to be removed not only from the package atmosphere but also from packaged meat itself. This makes a significant change of meat colour from oxymyoglobin red to myoglobin purple [9].

Issues that must be considered in any application of polymeric oxygen scavengers include removal of oxygen from the product and the package interior, reaction initiation, scavenger capacity, speed of oxygen removal, and the reaction products of the polymeric action which might possibly be either toxic or malodorous or both [9].

Desiccants have greater history than oxygen scavengers. The first applications used a sachet or capsule containing a desiccant that was placed inside the package.

Fig. 5.2 – Examples of sacheted desiccants

One of the first applications of desiccant additives in packages was in multilayer coextruded containers for retorted oxygen-sensitive food products. One of the best oxygen barrier plastics is water sensitive ethylene vinyl alcohol (EVOH). Burying the EVOH in an inner layer, surrounded by plastics such as LLDPE or PP which are good moisture barriers, maintains the protection at adequate levels in most instances. But during retorting the EVOH can pick up significant quantities of moisture. A solution to this problem was the incorporation of a desiccant in the tie layers between the EVOH and the main structural polymer in the package. Most moisture penetrating through the structural polymer, either from the steam heating on the outside or the moisture of the product on the inside, is captured by the desiccant.

5.1.2 CO_2 Scavengers

Carbon dioxide is formed in some foods due to deterioration and respiration reactions. The produced CO_2 has to be removed from the package to avoid food deterioration and/or package destruction. Unless removed, the generated CO_2 can cause the packaging to burst due to the increasing internal pressure.

The reactant commonly used to scavenge CO_2 is calcium hydroxide, which, at a high enough water activity, reacts with CO_2 to form calcium carbonate. A disadvantage of this CO_2 scavenging substance is that it scavenges carbon dioxide from the package headspace irreversibly and results in depletion of CO_2 which is not always desired. CO_2 scavengers are often included in oxygen scavenger or desiccant systems.

5.1.3 Antimicrobials or Biocides

Antimicrobial agents preserve compounded polymeric materials from attack by microorganisms such as bacteria, fungi, or mildews. Most synthetic polymers in their pure state are not attacked by

microorganisms; they are in general non-biodegradable. However, when various low molecular weight additives are compounded within the polymer, conditions for microorganism attack may be created. Plasticizers, lubricants, or heat stabilizers in the polymeric matrix can be the target of the microbial activity. Different additives pose different degrees of resistance to biodegradation.

Common preservatives used for polymers include 2-n-octyl-4 isothiazolin-3 and copper-8-quinoleate, in amounts ranging from 0.1-1 %. Antimicrobial agents for polymers are considered pesticides [1].

As for antimicrobial protection of packaged product are commonly used silver salts and organic compounds such as hinokotiol, but both of these and many others suffer from the fact that they only function in contact with the microorganism. The active package material must be in intimate contact with the microorganism on the food to be effective. Thus, microorganisms beneath the food surface or even on the surface but hidden in an irregularity cannot be harmed.

Solution is to incorporate a compound that volatilizes and thus can act at a distance and even below the surface of foods. Chlorine dioxide emitters in interleaving sheets have been reported to significantly reduce the microbiological count on and beneath the surface of the meat. Also ethanol, in low but effective quantities, demonstrated to be effective for microbial reduction on soft bakery goods [9].

5.1.4 Active packaging overview

Table 5.1 – Active packaging overview, removers, part 1

Packaging type	Examples of working principle" mechanism reagents	Purpose	Examples of possible applications
Oxygen absorbers (sachets, labels. films, corks)	Ferro-compounds, ascorbic acid, metal salts, glucose oxi-dases, alcohol oxidase	Reduction/preventing of mould, yeast and aerobic bacteria growth Prevention of oxidation of fats. oils, vitamins, colours Prevention of damage by worms, msects and insect eggs	Cheese, meat products, ready-to-eat products, bakery products, coffee, tea. nuts, milk powder
Carbon dioxide absorbers (sachets)	Calcium hydroxide and sodium hydroxide or potassium hydroxide Calcium oxide and silica gel	Removing of carbon dioxide formed during storage in order to prevent bursting of a package	Roasted coffee Beef jerky Dehydrated poul-try products
Ethylene absorbers (sachets, films)	Aluminium oxide and potassium permanganate (sachets) Activated carbon + metal catalyst (sachet) Zeolite (films) Clay (films) Japanese ova stone (films)	Prevention of too fast ripening and softening	Fruits like apples, apricots, banana, mango, cucumber, tomatoes, avocados and vegetables like carrots, potatoes and Brussels sprouts
Humidity absorbers (drip-absorbent sheets, films, sachets)	Polyacrylates (sheets) Propylene glycol (film) Silica gel (sachet) Clays (sachet)	Control of excess moisture in packed food Reduction of water activity on the surface of food in order to prevent the growth of moulds. yeast and spoilage bacteria	Meat. fish, poultry. bakery products, cuts of fruits and vegetables

Table 5.2 - Active packaging overview, removers, part 2

Packaging type	Examples of working principle mechanism rea gents	Purpose	Examples of possible applications
Absorbers of off flavours, amines and aldehydes (films, sachets)	Cellulose acetate film containing nar-inginase enzyme Ferrous salt and citric or ascorbic acid (sachet) Specially treated polymers	Reduction of bitterness in grapefruit juice Improving the flavour of fish and oil-containing food	Fruit juices Fish Oil-containing foods such as potato chips. biscuits and cereal products Beer
UV-light absorbers	Polyolefins like poly-ethylene and polypro-pylene doped the material with a UV-absorbent agent Crys-talliuity modification of nylon *6* UV stabiliser in poly-ester bottles	Restricting light-induced oxidation	Light-sensitive foods such as ham Drinks
Lactose remover	Immobilised lactase in the packaging material	Serving milk products to the people suffering lactose intolerance	Milk and other dairy products
Cholesterol re-mover	Immobilised choles-terol reductase in the packaging material	Improvmg the healthi-ness of milk products	Milk and other dairy products

In Table 5.2 are examples of sachet, label and film type absorbing (scavenging) active packaging systems for preservation and shelf-life extension of foods or improving their quality and usability for consumers. Oxygen, carbon dioxide, ethylene and humidity absorbers have the most significant commercial use, lactose and cholesterol removers are not yet in use.

In Table 5.3 examples of sachet and film type releasing active packaging systems for preservation and shelf-life extension of foodstuffs or improving their quality. So far, none of these systems are in wide commercial use [4].

Table 5.3 - Active packaging overview, emitters

Packaging type	Examples of working principle/ mechanism/reagents	Purpose	Examples of possible applications
Carbon dioxide emitters (sachets)	Ascorbic add Sodium hydrogen carbonate and ascorbate	Growth inhibition of gram-negative bacteria and moulds	Vegetables and fruits, fish, meat, poultry
Ethanol emitters (sachets)	Ethanol water mixture absorbed onto srlicon dioxide powder generating ethanol vapour	Growth inhibition of moulds and yeast	Bakery products (preferably heated before consumption) Dry fish
Antimicrobial preservative releasers (films)	Organic acids, e.g. sorbic acid Silver zeolite Spice and herb extracts Allylisothiocyanate Enzymes, e.g. lyzozyme	Growth inhibition of spoilage and pathogenic bacteria	Meat, poultry, fish, bread, cheese, fruit and vegetables
Sulphur dioxide emitters (sachets)	Sodium metabi sulfite incorporated in microporous material	Inhibition of mould growth	Fruits
Antioxidant releasers (films)	BHA BHT Tocopherol Maillard reaction volatiles	Inhibition of oxidation of fat and oil	Dried foodstuffs Faf-contaming foodstuffs
Flavouring emitters (films)	Various flavours in polymers	Minimisation of flavour scalping Masking off-odours Improving the flavour of food	Miscellaneous
Pesticide emitters (the outer or inner layer of packaging material)	Imazalil Pyrethrins	Prevention of growth of sporlage bacteria Fungicidal or pest control	Dried, sacked foodstuffs, e.g.. flour, rice, grains

Table 5.4 – Physical environment modifiers, antimicrobials

Packaging type	Examples of working principle/ mechanism reagents	Purpose	Examples of possible apphcations
Insulating materials	Special non-woven plastic with many air pore spaces	Temperature control for restricting microbial growth	Various foods to be stored refrigerated
Self-heating aluminium or steel cans and containers	The mixture of lime and water	Cooking or preparing food via built-in heating mechanism	Sake, coffee, tea, ready-to-eat meals
Self-cooling alumimum or steel cans and containers	The mixture of ammonium chloride, ammonium nitrate and wafer	Cooling of food	Non-gas drinks
Microwave susceptors	Aluminium or stainless steel deposited on substrates such as polyester films or paperboard	Drying, crisping and ultimately browning of microwave food	Popcorn, pizzas, ready-to-eat foods
Modifiers for microwave heating	A series of antenna structures that alter the way microwaves arrive at the food	Even heating, surface browning, crisping and selective heating	As above
Temperature-sensitive films	The gas permeability of the polymer is controlled by filler content, particle size of the filler and degree of stretching of the film	To avoid anaerobic respiration	Vegetables and fruits
UV-irradiated nylon film	The use of excimer laser 193 nm UV irradiation to convert amide groups on the surface of nylon to amines	Growth inhibition of spoilage bacteria	Meat, poultry, fish, bread, cheese, fruit and vegetables
FreshPad	Releasing natural volatile oils, absorbing oxygen and excess juice	Growth inhibition of bactena Moisture control Shelf-life improvement	Meat
Surface-treated food packaging materials	Fluorine-based plasmas	Growth inhibition of bactena	

5.2 Machinery and Technology

5.2.1 Mixed matrix

To achieve higher order barrier enhancement is mixed matrix produced by blending incompatible organic or inorganic compounds with polyolefins followed by orientation to produce a heterogeneous film. This makes passage of gases very hard and thus significantly improves the gas barrier properties of the substrate.

Among the materials that have been demonstrated to deliver the desired results have been nylon or mica platelets, or now nanocomposites such as montomorillonite in polyethylene or other polymeric substrates. Depending on the filler and its aspect ratio, orientation, density, etc. and the substrate, very significant gas and particularly oxygen barrier increases can be generated.

5.2.2 Nanolayer and microlayer coextrusion

Nanolayer and microlayer coextrusion is a method for combining two or three polymers as hundreds or thousands of alternating layers with individual layers as thin as tens of nanometers.
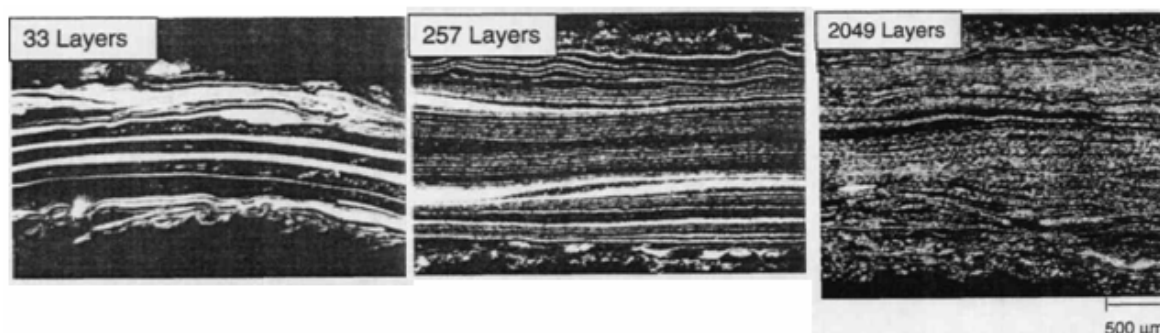
Fig. 5.3 – 33, 257 and 2049 layered microlayer blend

The possibility for utilizing microlayer coextrusion as a tool for creating microplatelets of high aspect ratio was explored. Polypropylene (PP) was combined with polyamide-66 (PA66) in microlayers. A high volume fraction of PA66 microplatelets dispersed in PP was achieved by injection moulding the micro-layered materials at a temperature intermediate between the melting points of the two constituents.
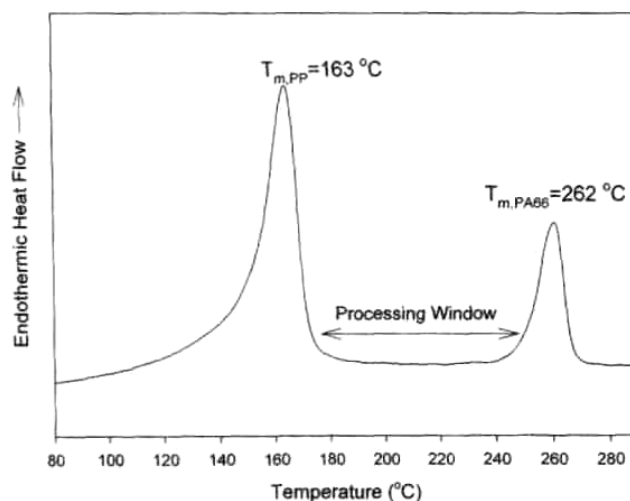
Fig. 5.4 – Processing temperatures of microlayer

coextrusion

The difference in melting temperatures provided a broad processing window of about 60 °C in which the PP layers melted to form the matrix whereas the PA66 layers remained in the solid state as dispersed microplatelets of high aspect ratio. The resulting material had significantly improved oxygen barrier properties. An enhancement of 4-5 times over the barrier of the conventional melt blend resulted from increased tortuosity of the diffusion pathway. [13]

Processing conditions and barrier properties are shown in Table 5.5, where p – permeability D – Diffusivity S – solubility

Table 5.5 – PP/gPP/PA66 microlayers properties

| Material	Blending Method	Processing Method	Processing Temperature (C)	Nominal Layer Thickness[a] (μm)	p[b]	D[c]	S[d]
PA66	NA	Extrustion	280	NA	0.064 ± 0.003	0.020 ± 0.002	0.038 ± 0.002
PP	NA	Injection Molding	180	NA	7.51 ± 0.06	1.45 ± 0.02	0.060 ± 0.001
PP/gPP/PA66 65/10/25	Microlayer 33 layers	NA	NA	25	0.30 ± 0.03	0.10 ± 0.01	0.037 ± 0.001
	Microlayer 33 layers	Injection Molding	180	25	1.04 ± 0.06	0.27 ± 0.03	0.045 ± 0.003
	Microlayer 257 layers	Injection Molding	180	2	0.96 ± 0.03	0.22 ± 0.01	0.049 ± 0.001
	Microlayer 2047 layers	Injection Molding	180	0.5	0.99 ± 0.02	0.23 ± 0.01	0.049 ± 0.001
	Microlayer 257 layers	Injection Molding	240	2	1.00 ± 0.11	0.23 ± 0.01	0.050 ± 0.002
	Microlayer 257 layers	Injection Molding	280	NA	3.97 ± 0.08	0.87 ± 0.01	0.053 ± 0.001
	Melt Extrusion	Compression Molding	280	NA	4.45 ± 0.04	0.95 ± 0.06	0.054 ± 0.003
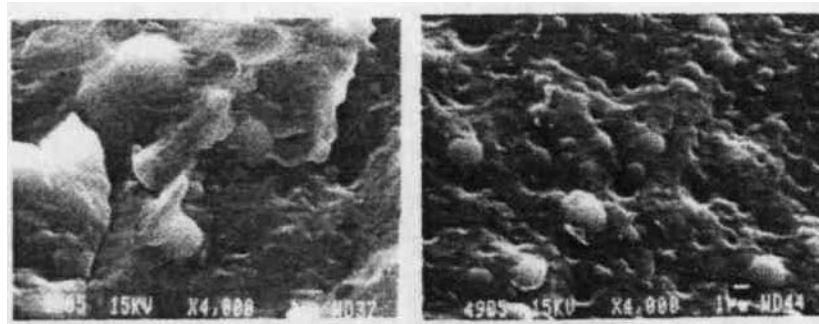
Fig. 5.5 – Visual comparison of dry blend (left) and microlayer (right)
structure

The concept of using nano-layer and microlayer coextrusion as a blending tool is an interesting new way to obtain novel solid-state structures. Despite the large difference in melt viscosities, it was possible to combine polypropylene and polyamide-66 as microlayers with more than 2000 layers and nominal layer thicknesses as small as 0.5 µm. Retention of the layered PA66 structure during subsequent injection moulding proved this to be a viable route to finished parts containing dispersed microplatelets and nanoplatelets. The difference in melting points provided a broad processing window in which the PP layers melted to form the matrix whereas the PA66 layers remained in the solid state as dispersed microplatelets. [13]

5.2.3   80-layer film coextrusion

A flat-die system that is said to produce films and coatings with a far greater number of layers than are produced by conventional coextrusion-yielding microlayer structures that improve moisture-barrier and gas-barrier capabilities, encapsulate gels and "unmelts", and enable more economical use of high-cost materials-has been developed by The Dow Chemical Co. and licensed from Dow by Extrusion Dies Industries (EDI).

Three or more extruders feed melt streams into an EDI-streamlined feedblock, which produces a uniform multilayer sandwich; this in turn is fed into a layer-multiplier device built by EDI using Dow's design. In this device, the layers are multiplied in stages. For example, three layers are multiplied into 12, which are multiplied into 48. The finished microlayer structure is then distributed in an EDI coextrusion manifold to achieve the desired product width. A practical upper limit has not been established, but the company estimates it is possible to produce 50-micron film with 80 layers.

EDI's microlayer technology integrates the Dow "layer multiplier into a complete custom-engineered system that includes the die, feedblock, and other tooling components for distributing the complex structure into a finished extrudate. EDI will license the Dow technology [14].

5.2.4   Cyclic olefin copolymer layers

The clarity, purity, and mechanical properties of COC films help improve packaging for foods, pharmaceuticals and other consumer products. The low water absorption and low permeability of COC films make them ideal in situations where a moisture barrier is needed. COC can be processed as monolayer or multilayer films for use in shrink wrap, pouches, laminates, and coextruded packaging structures.

Table 5.6 – COC properties

COC physical properties	Available Grades*				
	A	B	C	D	E
Melt flow index at 260°C, g/10 min	30	55	16	16	12
Density, g/cc	1.02	1.02	1.02	1.02	1.02
Water absorption, %	<0.01	<0.01	<0.01	<0.01	<0.01
Mold shrinkage, %	0.6-0.7	0.6-0.7	0.6-0.7	0.6-0.7	0.6-0.7
Tensile strength, psi	9570	9570	9570	9570	9570
Elongation @ break, %	10	3	4	4	4
Tensile modulus, kpsi	377	449	464	464	464
Charpy impact, kJ/m	13	15	15	15	15
Notched Charpy impact, kJ/m^2	2.6	1.7	1.7	2.0	2.0
HDT @ 66 psi, °C (°F)	75 (167)	130 (266)	130 (266)	150 (302)	170 (338)
Dielectric constant at 1–10 kHz	2.35	2.35	2.35	2.35	2.35
Comparative tracking index	>600	>600	>600	>600	>600
Volume resistivity, ohm-cm	>10^{16}	>10^{16}	>10^{16}	>10^{16}	>10^{16}
Light transmission, %	92	92	92	92	92

*Grades correspond to Ticona's Topas COC: A – 8007, B – 5013, C – 6013, D – 6015, E – 6017

As for environmental compatibility and consumer safety issues, the U.S. FDA has issued a regulation for ethylene-norbornene copolymers in dry-food-contact, which amends that part of the federal Food, Drug and Cosmetic Act concerned with polyolefins (21 CFR177.1520). COC from Ticona complies fully with this act and all applicable food additive regulations for aqueous, acidic, fatty, and low-alcohol and high-alcohol foods. COC is also suitable for many food-contact applications in Europe, where the monomers used in its manufacture are listed in applicable European Union directives [1].

CONCLUSION

Packaging materials are becoming more and more ingenious. They have evolved from simple PE film wrap to special purpose self-caring and modifying active packaging that is designed to maximize product life. Special blends are prepared to match exact needs, coextruded film with even 80 layers are being coextruded. The progress is substantial.

Multilayer structures are being completed in more sophisticated way, including more layers and even excluding tie layers of adhesives thus simplifying processing and maintaining properties. Most used multilayer films used in packaging are using polyolefin outer layers and polyamide or EVOH barrier core.

Active packaging is one of the most evolving branches of packaging industry. It is highly important, because without scavenging and optimizing, even the most sophisticated package would be in some cases worthless, because for instance fresh food or meat tends to deteriorate in oxygen or CO_2 environment. Even when the package is evacuated and tightly packed in barrier film to prevent permeation from the outside, the packed goods can emit these gasses itself by residual breathing process (fresh vegetables) or partial overtime decomposition.

When packaging containers are moulded, microlayer coextrusion blends of polyolefin matrix with incorporated barier platelets can be used to multiply barrier characteristics, making extremely tough way getting into the package.

At the conclusion it should be said that it was not really possible to cover everything which is involved in packaging industry nowadays, because there is an evolution in practically every way possible. There is a continuous need to improve these materials in physical, structural or chemical way. Brand new polymer blends and composites are coming to meet specific end-user requirements and including all these facts is nearly impossible.

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LIST OF SYMBOLS AND ABBREVIATIONS

AA   acrylic acid

aPA   amorphous polyamide

CO2   carbon dioxide

COC   cyclic olefin copolymer

CTT   Cold Total Transfer technology

D   diffusivity

EA   ethyl acrylate

EAA   ethylene acrylic acid

EDI   Extrusion Dies Industries

EMAA   ethylene methacrylic acid

EVA   ethylene vilnylacetate

EVOH   ethylene vinylalcohol

FDA   Food and Drug Administration

FFS   Form-fill-seal machine

HALS   hindered amine light stabilizers

HDPE   high density polyethylene

HMW-HDPE   high molecular weight- high density polyethylene

IBC   internal bubble cooling

LDPE   low density polyethylene

LLDPE   linear low density polyethylene

LLDPE-gMA   linear low density polyethylene grafted maleic anhy-

MA   maleic anhydride

MDPE   medium density polyethylene

mMDPE   metalocene medium density polyethylene

mPP   metalocene polypropylene

MW   molecular weight

MWD   molecular weight distribution

O2   oxygen

OPP   oriented polypropylene

p	permeability
PA	polyamide
PA6	polyamide 6
PA66	polyamide 66
PAO	poly-alpha-olefin
PE	polyethylene
PEI	polyethylene imine
PET	polyethylene terephtalate
PP	polypropylene
PS	polystyrene
PVA	polyvinylacetate
PVDC	polyvinylidenchloride
PVOH	polyvinylalcohol
RH	relative humidity
S	solubility
SPPF	solid phase pressure forming
Tg	glass transition temperature
Tm	melting temperature
ULDPE	ultra low density polyethylene
UV	ultra-violet
VA	vinylacetate
VOH	vinyl alcohol
WVTR	water vapour transition rate

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