3 Polymers Used in Flexible Packaging

3.1 Types of Polymers

Flexible packaging uses a wide range of materials, including plastic films, paper, and aluminum. The plastic films include various types of vinyl polymers, polyesters, and polyamides. The used polymers are homopolymers, copolymers, or polymer blends, and are usually compounded with various additives (e.g., antioxidants, plasticizers, moisture absorbers, colorants, and the like) to improve certain properties. The films are used either as a single layer or as coextruded multilayers. The films are also commonly coated, metalized, or otherwise treated to enhance the performance of the resulting package. Flexible packaging materials are selected based on a variety of factors, including desired barrier properties, mechanical performance, cost, sealing properties, appearance, physical feel, printability, and easy opening/reclosing features. While there are many polymers utilized in the flexible packaging industry, the most common ones are polyolefins, including the various types of polyethylene and polypropylene, poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC) [1,2].

Each polymer used in flexible packaging is examined in terms of sustainability and recyclability.

3.2 Polyolefins

The polyolefins[1] is a group of vinyl polymers, which comprise more than 50 wt% monomers based on the weight of the polymer derived from one or more olefin monomers, for example, ethylene or propylene, and, optionally, may contain at least one comonomer. They are produced mainly from nonrenewable fossil fuel-based resources. Their easy processability, low price, chemical inertness, good optical properties, flexibility, and toughness have made them the most versatile polymers in the packaging industry and distribution of products. Polyolefins are suitable

[1] They are also called *polyalkenes*.

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for packaging of single or bundle packaging of food and other products, such as cosmetics, toys, stationery, confectionery, chemicals for households, etc. They are also prone to thermo-fusion welding.

Flexible polyolefin packaging films have the disadvantage that they are not receptive to printing inks. Therefore, practical films of this type have coatings or surfaces specially treated (e.g., by corona treatment).

Polyolefins are naturally hydrophobic, and they do not decompose in the environment.

3.2.1 Polyethylenes

Polyethylenes are a group of ethylene polymers, which comprise more than 50 wt% ethylene monomer. Polyethylene films are by far the largest volume flexible packaging film family accounting to more than 32% of the total market share.

Polyethylenes are available with a wide range of properties combining transparency (low-density types), toughness, heat seal-ability, low water vapor transmission rate, low-temperature performance, and low cost. Polyethylene films are highly permeable to oxygen and other nonpolar gases and have high viscoelastic flow properties. Polyethylene has the lowest softening point of the basic packaging polymers. The lower softening point results in lower processing energy costs. Polyethylene can be clear or translucent depending on density. It is a tough, waxy solid that is unaffected by water and is inert to a large range of chemicals. The properties of polyethylene are highly dependent on type and number of chain branches. Polyethylene is marketed in three general categories: low, medium, and high density.

3.2.1.1 Low-Density Polyethylene

Low-density polyethylene (LDPE), also referred as "high pressure polyethylene" or "highly branched polyethylene", is characterized by a high degree of short- and long-chain branching, which contributes to its relative processing ease. It has a density in the range of 0.916−0.930 g/cm^3 and a melting temperature of 105−115°C and can be processed at low temperatures and pressures while maintaining a good melt strength.

LDPE is blown, slit, and wound to create film rolls, which is increasingly used by product manufacturers for a variety of packaging purposes, such as plastic bags and shrink film. Most stock poly bags used to wrap a large variety of products are made from LDPE. LDPE is widely used for shrink bundling, offering low shrink temperature and excellent clarity. One of the most common uses for LDPE bundling film is for wrapping water bottles and canned goods. The LDPE bundling film is thicker and offers more strength than PVC shrink film.

LDPE film is used mainly for its heat-seal ability and bulk in packaging. LDPE film is flexible and tough. The toughness and durability of LPDE film offer several advantages:

- stability for unsupported and bundled products;
- good tear resistance;
- a coefficient of friction that helps the film form to the product's shape and holds it in place during stacking or stretch wrapping prior to distribution;
- low cost and recyclability that makes it a sustainable option for many manufacturers [3].

LDPE film also has some limitations to consider:

- poor weathering resistance;
- poor gas barrier properties;
- low tensile strength;
- limited possibilities for down-gauging (reducing the thickness), due to a low draw ratio, and low stiffness of the polymer;
- can appear cloudy, depending on the level of technology used during its manufacture [3].

LDPE film can be collected and recycled to create new products, such as piping, trash bags, sheeting, and films for building and agricultural applications, composite lumber, and other products [3].

3.2.1.2 Linear Low-Density Polyethylene

Linear low-density polyethylene (LLDPE) includes linear, substantially linear or heterogeneous copolymers of ethylene with α-olefins, usually 1-butene, 1-hexene, or 1-octene. LLDPE contains less long chain branching than LDPE and is tougher and has better heat-seal strength than LDPE. It has a density in the range of 0.915–0.934 g/cm^3 and a melting temperature of 115–125°C. Its stiffness, however, remains low and its processability is well below that of LDPE. Also, conventional LLDPE's optical properties do not match those of LDPE. Optical properties of LLDPE have been improved by using metallocene-catalyzed LLDPE (mLLDPE); however, the processability of these grades is generally worse than that of conventional LLDPE (2000, US6114456, FINA RESEARCH).

Most stretch films are made from either cast or blown extruded LLDPE. LLDPE offers the high stretch rate needed for stretch film. Because of the strength and stretch characteristics of LLDPE, such film is used as a baling material and wrap material for palletized loads or bailing processes. LLDPE film wraps and secures bottles, other containers, or similar items on a pallet during shipping. The LLDPE film typically is wrapped around the materials on the pallets several times so that there are layers upon layers of the film. Upon arrival at a given destination, the LLDPE is removed from the palletized materials and scrapped. LLDPE film is also used to baling waste material. When LLDPE film is removed from the pallets or other bales, because of the high level of contamination, such as dirt, oil, biological material, layering, label adhesives, etc. the LLDPE film is either disposed in a landfill or processed as a filler for other plastic products. Reuse of the LLDPE film as a viable blown film product for use as an industrial film or a bag product has generally not been instituted. Typically, such used film has limited use due to high level of contamination present which, in turn, causes severe processing issues as well as unpleasant properties in the finished product, for example, odor, discoloration and “pitted” appearance (2014, **WO2014158316** A1, WISCONSIN FILM & BAG INC).

3.2.1.3 Very Low-Density Polyethylene

Very low-density polyethylene (VLDPE)[2] is a substantially linear polyethylene comprising, like LLDPE, only copolymers of ethylene with α-olefins, usually 1-butene, 1-hexene or 1-octene, and having a high degree of linearity of structure with short branching rather than the long side branches characteristic of LDPE. Today’s commercially available VLDPEs are metallocene-catalyzed (mVLDPEs) of narrow molecular weight distribution; they are produced in a gas phase process and provide high film toughness (Dart Impact Strength $>$ 450 g/mil for a 1 mil monolayer film), but tend to have a number of drawbacks. Due to their narrow molecular weight distribution, mVLDPEs have difficulty in conversion to finished products, and the prepared films have the tendency to split in the machine direction. In addition, both the mVLDPEs and the

[2] Also called ultra low-density polyethylene (ULDPE).

Ziegler−Natta catalyzed (z-nVLDPEs) demonstrate nonhomogeneous melting of the VLDPE copolymer, i.e., exhibiting at least two peaks in the Differential Scanning Calorimetry (DSC) measurement (2016, **WO2016027194** A1, NOVA CHEM INT SA).

VLDPE has been used for making shrinkable mono- or multilayer films for food packaging (1996, **EP0374783** A2, VISKASE CORP). A commercial VLDPE for flexible packaging is Exceed™ 1012 CA of Exxon Mobil Chemical Company, which is an mVLDPE having a density of 0.912 g/cm^3 and outstanding toughness [4].

3.2.1.4 Medium-Density Polyethylene

Medium-density polyethylene (MDPE) has a density in the range of 0.926−0.940 g/cm^3 and a molecular weight distribution greater than 2.5. MDPE offers much improved rigidity and down-gauging possibilities. MDPE is translucent, lacking the good optical properties of LDPE or LLDPE (1998, **EP0870802** A1; and 2000, **US6114456**, FINA RESEARCH). MDPE is the least commonly used polyethylene for flexible film.

3.2.1.5 High-Density Polyethylene

High-density polyethylene (HDPE) has little branching, which gives it stronger intermolecular forces and tensile strength than LDPE. It has a density in the range of 0.941−0.970 g/cm^3 and melting temperature of 125−135°C. Further, it has excellent puncture resistance, low stretch, reduced tearing, and moisture protection. HDPE has much higher stiffness, higher temperature resistance, and much better water vapor barrier properties than LDPE, but it is more opaque and can withstand somewhat higher temperatures (120°C for short periods) [5].

HDPE finds uses in industrial wrapping and packaging. Many retail bags are made from extruded HDPE (2−10 mils thick). Common products include grocery bags, T-shirt bags, packaging films, trash bags, bags with sealed air for packaging (e.g., air cushion), and a large selection of retail packaging bags. HDPE is also used for making woven sacks/bags.

Recycled HDPE film is primarily used for composite lumber and plastic bags [3].

3.2.1.6 Ethylene-Vinyl Acetate

Ethylene-vinyl acetate (EVA) is a polar copolymer of ethylene and vinyl acetate, retaining some of the properties of polyethylene, but with increased flexibility, elongation, and impact resistance. EVA is often used as extrusion coating on polypropylene, aluminum foil, and PET, to provide good heat-sealing at high converting rates, or as an adhesion layer in some laminates. Important applications in flexible packaging include sealants in meat and dairy packaging structures.

Elvax® EVA (Dow, ex DuPont) is an inherently flexible, tough and clear resin that is used as a heat seal layer, coextrusion tie layer, or structural layer. It can be made into blown or cast monolayer and coextruded films [6]. Elvax® can be blended into polyethylene to improve end-use properties, especially at low temperatures, for frozen food and ready-to-eat food packaging applications. Its low seal initiation temperature and ability to seal to themselves and other substrates allow for higher line speeds and help reduce package failures. Typical structures for fresh meat barrier packaging and block cheese packaging are EVA/PVDC/EVA and PE/EVA/PVDC/EVA/PE [7].

3.2.1.7 Ethylene-Vinyl Alcohol

Ethylene-vinyl alcohol copolymer (EVOH) is a flexible, crystal clear, and glossy thermoplastic ethylene copolymer in which varying amounts of the −OH functional group have been incorporated. A typical packaging EVOH consists of about 20%−35% ethylene. It has excellent flex-crack resistance, and very high resistance to hydrocarbons, oils, and organic solvents. EVOH has been one of the most effective gas barrier materials known to the flexible packaging industry, especially in providing an excellent barrier for oxygen and aroma. EVOH is extensively used in modified atmosphere packaging (MAP), where a certain atmosphere is needed inside the package to improve the shelf life of food products. Other applications include medical and pharmaceutical packaging.

A multilayer packaging film, including an EVOH layer, is often subject to a heating treatment (retort treatment or boiling treatment) with hot water or water vapor for a long time period, often carried out after filling the packaging materials with contents, such as foods. EVOH results in a problem through the heating treatment involving resin whitening and/or deterioration of the capability to keep the shape of the vacuum-packed contents. Various techniques have been developed to address this problem (2017, **EP3144349** A1, KURARAY CO LTD).

EVOH loses its gas barrier property when exposed to a high moisture environment. Therefore, EVOH requires a moisture barrier layer for protection, such as a nonpolar layer or metalized layer. In order to optimize both cost and performance, EVOH is frequently used in multilayer, coextruded films, such as LDPE, HDPE, polypropylene, and PET, which have superior moisture barrier properties. However, the polar EVOH is not compatible with a nonpolar polyolefin film, such as biaxially oriented polypropylene (BOPP). Thus, it requires an adhesion promoter or tie-layer resin, such as anhydride-modified polyolefin in order to adhere to a nonpolar polyolefin substrate.

EVOH has a melting temperature of 165−185°C. This can cause problems in the recycling process if different materials melt at different temperatures [8]. An EVOH barrier layer sandwiched between polyethylene layers has the tendency to gum up when reprocessed, resulting in holes in the recycled polyethylene film [9].

Kuraray's EVOH filmgrades of EVAL™ combine the humidity resistance and easy processing of ethylene with the exceptional gas barrier and resistance to organic solvents of poly(vinyl alcohol) (PVOH) [10]. Representative flexible multilayer structures of EVAL™ finding applications in food packaging are:

fresh meat shrink wrap: PA/EVAL™/PA/tie/PE;

sliced ham: PET/tie/EVA™L/PA/tie/EVA;

MAP with long-lasting gas mix: PET/PE/tie/EVAL™/tie/EVA;

UHT[3] milk pouch: PE/tie/EVAL™/tie/PE; and

transparent packs for sensitive foods: OPP/EVAL™/PE.

Another commercial EVOH for flexible packaging is Soarnol™ developed by Nippon Gohsei and owned by Mitsubishi [11]; and Evasin® EVOH copolymers of Chang Chun Petrochemicals, marketed by Arkema [12].

3.2.2 Polypropylene

Polypropylene is a tough and rigid thermoplastic polymer with properties similar to polyethylene. It has a low cost and is the second-most widely produced commodity plastic (after polyethylene). It has a density in the range of 0.895−0.92 g/cm^3, the lowest among commodity polymers, and a melting point of 130−170°C; commercial isotactic polypropylene has a density in the range of 0.900−0.905 g/cm^3 and a melting point in the range of 160−166°C. Depending on the desired

[3] Ultra-high temperature or ultra-heat treatment, or ultra-pasteurization.

properties, different types of polypropylene are used, including homopolymers, random, heterophasic and random heterophasic co-polymers (Rahecos). Polypropylene homopolymers are characterized by high stiffness, excellent heat deflection temperatures, excellent moisture barrier, and good transparency, as well as high tensile strength for film applications. Random propylene copolymers with statistically incorporated ethylene monomer into the isotactic polypropylene chain are very soft and have excellent heat sealing properties at low sealing initiation temperature, very low-stress whitening and the best optical properties (gloss and haze) of all polypropylene grades. Heterophasic propylene copolymers have an ethylene-propylene rubber as a separate phase dispersed in a polypropylene homo- or copolymer matrix, and the films are characterized by a matt surface and low transparency. The high toughness and good stiffness over a very wide temperature range, are the dominant properties of this material. Rahecos comprise a propylene random copolymer matrix and an ethylene-propylene rubber and combine the properties of both previously mentioned propylene copolymers (2009, **WO2009019277** A1, BOREALIS TECH OY). A commercial product of the Rahecos propylene copolymers is Borsoft™ of Borealis, which can produce films with extreme softness and toughness [13].

The two most important types of polypropylene films are cast (unoriented) polypropylene (CPP) and biaxially oriented polypropylene (BOPP). Both types have a high gloss, exceptional optics, good or excellent heat-sealing performance, better heat resistance than polyethylene, and good moisture barrier properties. Nowadays, the majority of polypropylene films for packaging applications are made using the casting process, in particular, the chill roll process. Polypropylene films can be metalized, which results in improved gas barrier properties for demanding applications where long product shelf life is important. Polypropylene is also used for making packaging straps and woven sacks/bags. Polypropylene film composes over 20% of all film generated, and it is estimated that about 70% of it is generated in the residential sector [14].

Although industrial woven polypropylene slit film products are currently recycled, polypropylene films are not.

3.2.2.1 Cast Polypropylene

The main characteristics of cast polypropylene (CPP) film are high gloss finish, high clarity (transparency), increased rigidity, and high moisture barrier. Due to its unoriented manufacturing process, it is resistant to impact and low temperatures. The CPP film properties can be customized to meet specific packaging, performance, and processing requirements. In general, CPP has higher tear and impact resistance, better cold-temperature performance, and heat-sealing properties than BOPP. CPP generally finds fewer applications than BOPP. However, CPP has been steadily gaining ground as an alternative material in many traditional flexible packaging applications. CPP requires lesser fixed investment compared to BOPP film and is, thus, preferred by the packaging industry [15].

CPP films of 20−80 μm thick are widely used in the flexible packaging industry for applications, such as food (e.g., bread, snacks, and dried food), confectionery, beverage, textiles, cosmetics, pharmaceuticals, and others. Some typical packaging applications of polypropylene cast films are listed in Table 3.1.

3.2.2.2 Oriented Polypropylene

Polypropylene films are oriented or stretched in one direction (OPP) or in two directions (BOPP). This orientation of the film brings about several changes in the film, such as lower elongation, higher tensile strength, greater stiffness, improved optical properties, and better barrier to moisture/gases. Both OPP and BOPP are used in a wide variety of packaging applications, including use as packaging films and labels employed on plastic bottles.

An OPP film has linear and parallel tear properties. This property is used to open packaging films easily and conveniently. A commercial OPP film is Nowostraight of Nowofol Kunststoffprodukte GmbH & Co. KG. The notch on the side ensures that the film always tears in a linear and parallel direction [16,17].

The BOPP film is used for the purpose of various flexible packaging films or labels with high strength and excellent tensile, transparency, and water vapor barrier properties. These key properties, combined with an excellent cost/performance ratio, have made BOPP one of the most popular and highly demanded film packaging material for form-fill-seal packaging of food and nonfood. BOPP films are mainly used for the packaging of food products, such as snacks, bakery, confectionery, dried foods, and pasta/noodles. Dried food dominated the global BOPP film market in 2014 [18].

Some of the main players in the global BOPP film market include: Taghleef Industries, Jindal Poly Films, Nan Ya Plastics, Treofan, Vibac, Vitopel, Jiangsu Shukang Packing Material Co., Ltd., Futamura, Cosmo

Table 3.1 Typical Packaging Applications of Polypropylene (PP) Cast Films

Film Packaging	Type of Polypropylene	Properties	Exemplary Applications
Textile	Random copolymers with high C_2-content	Excellent sealing and optical properties	
Flower	Mono- or three-layer co-extruded films with PP homo-polymers and PP random copolymers	PP homopolymers: stiffness; PP random copolymers: sealing, optics	
Food	PP homopolymers, random copolymers, hetero-phasic copolymers, depending on required properties like	Good mechanical properties, excellent optics, low-temperature resistance, good sealing properties	
Laminating films	PP random copolymers and heterophasic copolymers for lamination with aluminum, other plastics films (PET, PA, PE)	Good sealing properties	

Courtesy of Borealis A/S. Polypropylene cast film; 2006. https://www.fist.si/datoteke/navigacija/PP-Cast-film.pdf.

Films, Kopa Films, Dow (ex DuPont; masterbatches for BOPP), Innovia Films, and Ampacet Corp. (masterbatches for BOPP) [18].

A variety of structures and compositions employed in commercial BOPP flexible packaging and label applications can be recycled, including structures based on clear, white, coated, or metalized films. The streams of reclaimed BOPP flexible packaging and label structures most often include inks, lacquers, coatings, and adhesives, which generally have been considered to render them undesirable for use as recycled material in plastic film structures; particularly, when a gray tint or hue is unacceptable (2007, **US2007120283** A1; and 2008, **US2008233413** A1, APPLIED EXTRUSION TECHNOLOGIES).

3.3 Polystyrene

Polystyrene, also known commercially as crystal polystyrene or general-purpose polystyrene, is an amorphous polymer and has the particular properties of high clarity, being colorless, hard, but rather brittle. Polystyrene film can be biaxially oriented, in this form maintains clarity, and overcomes some of the brittleness of unstretched plastic. Biaxially oriented polystyrene films in thin gauges are used for food packaging carton windows. They have also been used as breathable films for over-wrapping fresh produce, such as lettuce [19]. Polystyrene represents a niche market ($<1\%$ [20]) in monolayer and multilayer blown films because it is stiff, clear, and printable. It also has good dead-fold properties, and its gas transmission or "breathability" is an increasingly attractive property for packaging fresh foods [21].

3.4 Chloropolymers

Chloropolymers are vinyl polymers in which one or more hydrogen atoms have been substituted by chlorine. The most common members of this polymer class used in flexible packaging are PVC and PVDC.

3.4.1 Poly(Vinyl Chloride) (Plasticized)

The unmodified PVC is not particularly useful; it has very low thermal stability and degrades rapidly at temperatures required for processing ($>160°C$). Hence, PVC is compounded with various additives to improve its processing and performance characteristics. By the inclusion of plasticizers, PVC can be made soft and flexible. In this form, known as plasticized PVC (PVC-P), it can form films. PVC-P can be fabricated into a tough, puncture-resistant, clear, and low-cost packaging film product. The film has good cling and heat-seal properties. It is mainly used as cling and stretch film and in closures and repeat-use flexible tube applications [22]. Because PVC has a comparable low permeability to oxygen, it keeps food, such as meat and cheese fresh. A representative example of commercial PVC for the manufacture of cling film is SolVin® S-PVC of Solvay [23].

PVC has been under pressure on the grounds of health and safety concerns. Attention has been focused on the migration of residual vinyl chloride monomer and plasticizers from flexible PVC food packaging into the edible material. There have also been environmental concerns on the waste management of PVC [22].

The costs for the recycling of PVC films in packaging waste are considerably high. Generally, the collection of PVC packaging films and other PVC products in the EU is included in the existing packaging recycling systems. For the packaging recycling systems in Austria and Germany, the costs for the plastics fraction are between 700 and more than 1.000 €/ton. This is far from economic profitability [24]. Flexible PVC is also harmful to the incineration process, and in the Nordic countries, it is currently landfilled [25].

A major problem in the recycling of flexible PVC is the high chlorine content in raw PVC (about 56% of the polymer's weight) and the high level of plasticizer added to the polymer. As a result, PVC requires separation from other plastics before mechanical recycling.

3.4.2 Poly(Vinylidene Chloride)

Poly(vinylidene chloride) (PVDC) is a chloropolymer that has excellent barrier properties to a wide variety of gases and liquids due to the combination of high density and high crystallinity. Coated or extruded PVDC with superior resistance to most gases, particularly oxygen and moisture vapor, is used in packaging. An OPP film-coated or coextruded with PDVC is a particularly good flexible packaging material for products, which tend to be sensitive to attack by oxygen, such as, for example, coffee and cheese, or snack foods, such as corn-based products and potato chips. Additionally, PVDC top-coating materials promote the heat sealability of such oriented film structures which, in an uncoated state, tend to seal only with great difficulty, if at all (1994, **US5286424** A, MOBIL OIL CORP).

PVDC has a number of limitations due to its poor thermal stability. Its degradation begins at about 120°C, and its extrusion temperature is in the range of 150−180°C. It is prone to gel and black spec formation during high-temperature extrusion, and evolves corrosive by-products, which require special materials of construction and good ventilation, and is known to discolor when exposed to radiation [26].

The PVDC must be stabilized and plasticized in order to be successfully extruded at commercial rates; typically used stabilizers-plasticizers are epoxidized oils.

Although PVDC is an excellent gas barrier polymer, it is being phased out of many packaging applications because of environmental concerns [27]. PVDC layers and coatings render a flexible plastic packaging, nonrecyclable according to APR (Association of Plastic Recyclers) test protocols [28]. Specifically, PVDC is not compatible with polypropylene films or labels into which the plastic films are intended to be recycled (see also Table 3.4), and tends to release chlorine or HCI when melted causing all the other materials to degrade besides causing atmospheric pollution. The removal of PVDC from the plastic films prior to recycling them is costly, and therefore, economically not feasible (2007, **US2007120283** A1; and 2008, **US2008233413** A1, APPLIED EXTRUSION TECHNOLOGIES).

The main producers of PVDC are SK Global Chemical[4] [29], Solvay [30], Kureha [31], Asahi Kasei [32], Juhua Group, Nantong SKT and Keguan Polymer.

3.5 Poly(Vinyl Alcohol)

Poly(vinyl alcohol) (PVOH) is a biodegradable fossil fuel-based vinyl polymer used in food packaging applications because of its high barrier properties to oxygen and carbon dioxide. On the other hand, its mechanical and water resistance is limited. PVOH is water-soluble, and therefore, is sometimes combined with other polymers and put in the core layer of a multilayer packaging structure. PVOH, as well EVOH, are highly hygroscopic materials and lose their barrier properties when they absorb water. PVOH has been replaced by EVOH because it is more expensive and its processability is more challenging than EVOH.

[4] SK Global Chemical, the chemical unit of SK Innovation, acquired in 2017 Dow’s PVDC unit.

Detergent packaging is the dominant application of PVOH because of its water solubility, and nonhazardous and nontoxic properties. Laundry detergents are, nowadays, packaged in PVOH films in the form of small packs named water-soluble pods. PVOH films are also suitable for manufacturing bags for agrochemicals.

Main manufacturers of PVOH films include Nippon Synthetic Chemical Industry Co., Ltd., Kuraray Co., Ltd., and Sekisui Chemical Co., Ltd., and others. During the past few years, the global market has observed a considerable rise in the production capacity of PVOH films [33].

3.6 Polyesters

Aromatic, semi-aromatic and aliphatic polyesters are used in flexible packaging as mono- or multilayers, coatings, and adhesives.

3.6.1 Aromatic Polyesters

Among the aromatic polyesters, the most widely used polyester in flexible packaging is PET.

3.6.1.1 Poly(Ethylene Terephthalate)

PET possesses excellent high-temperature properties, high strength, and clarity, and has moderate oxygen and carbon dioxide barrier properties. In particular, biaxially oriented polyester (BOPET) film is an important material in the field of flexible packaging because of excellent balance between cost and mechanical strength, heat resistance, dimensional stability, chemical resistance, and optical properties. BOPET films find applications in flexible packagings, such as bags and pouches for food products, wrapping of food and confectionery, or shrink labels for bottles.

3.6.1.2 Poly(Ethylene Furanoate)

Poly(ethylene furanoate) (PEF) is a 100% biobased polyester, which has the potential to replace PET in the future. A PEF film has better gas barrier properties than PET (at least six times for oxygen, three times for carbon dioxide, and two times for moisture vapor).

PEF is currently in the development stage. At present, the focus is on soda and water bottles, but applications for flexible films with a good gas and odor barrier will follow (2016, **WO2016032330** A1, FURANIX TECHNOLOGIES BV). Toyobo (JP) and Avantium (NL) (FURANIX, SYNVINA) developed PEF-based thin films about 10 μm thick, which can be applied for food packaging, and in industrial and medical packages (2018, **EP3398768** A1, TOYO CO LTD; SYNVINA CV).

PEF can be mixed with its fossil fuel-based counterparts, e.g., industrial PET, and recycled in existing recycling facilities. PEF would be compatible in an amount up to 2% in the existing PET recycling stream [16,17].

3.6.1.3 Semi-Aromatic Polyesters

These biodegradable polyesters are predominantly derived from fossil fuel-based resources. The most commonly used semi-aromatic polyester is poly(butylene adipate-*co*-terephthalate) (PBAT), which is nonbiobased and fully biodegradable. The PBAT produced by BASF under the trademark of Ecoflex is a flexible plastic designed for film extrusion and extrusion coating.

PBAT is used for the toughening of PLA and starch while maintaining biodegradability. Ecovio produced by BASF is a blend of Ecoflex and PLA used in film applications, such as cling film, shopping bags, and compost bags. PBAT reduces the stiffness and improves the tear strength of a PLA-based flexible film [34]. PBAT improves the processability, water resistance, and tear strength of starch-based flexible films [34]. Origo-Bi produced by Novamont is a blend of PBAT with starch.

3.6.2 Aliphatic Polyesters

Aliphatic polyesters are biodegradable polymers derived from either renewable (biobased) or fossil-fuel (nonbiobased) resources. The most important group of biodegradable aliphatic polyesters are the biobased ones.

3.6.2.1 Poly(hydroxy acid)s

The poly(hydroxy acid)s are biodegradable aliphatic polyesters synthesized from hydroxy acids and/or esters or by ring-opening polymerization of cyclic esters.

The most widely used poly(hydroxy acid) is the biobased poly(lactic acid) or polylactide (PLA) that is derived from lactic acid, or preferably from lactide (a lactic acid dimer). There are two forms of lactic acid (D- or L-lactic acid). The properties of PLA can be varied by adjusting the relative amounts of the two lactic acid isomers in the polymer. A PLA formulation of about 90% L-lactic acid and 10% D-lactic acid is commonly used for the production of packaging films. PLA has reasonable moisture and oxygen properties and is suitable for various flexible packaging, such as blown and cast film. PLA films are not as flexible as LPDE films, but rather stiff (comparable to PET and cellophane). PLA is currently used in wraps for bakery and confectionery products, containers for fresh produce, etc. [35]. The rate of degradation of PLA depends on the degree of crystallinity. Increasing the amount of D-isomer in predominantly L-PLA tends to suppress crystallinity and therefore increase the rate of biodegradation [36] (see also Chapter 10, Section 10.2.4).

Nativia films is a range of bio-based and biodegradable (PLA) packaging films produced by Taghleef Industries. The film is used for the packaging of products ranging from bakery items to pet food [37].

Nativia Ness of Taghleef Industries is a potato starch- and PLA-based white voided biobased film. The film was originally designed for wrapping chocolate bars of Mars in cooperation with Mondi and Rodenburg Biopolymers.[5] The starch-based candy wrapping of Mars can replace the current BOPP film used in chocolate bar wrappers [38].

3.6.2.2 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) is a family of biodegradable aliphatic polyesters produced by microorganisms. The properties of a PHA can be altered by copolymerization with more than 150 different monomers within this family. PHAs are limited to very small-scale applications in packaging, mainly because of their higher price versus fossil fuel-based polymers. In addition, most PHAs types are brittle.

The most common PHA is poly(3-hydroxybutyrate) (PHB). The structure of PHB is comparable with that of isotactic polypropylene, and hence, it has many similar properties similar to polypropylene. The isotacticity combined with the linear nature of the chain results in a highly crystalline material with very attractive strength and modulus, but very poor elongation (3%). PHB films cannot be made by conventional processing due to their low elongation. PBAT was blended with PHB to increase its elongation, and thus, make it feasible to process blown film and also the addition of flexible PBAT to PHB was successful in increasing the toughness.

The challenges in processing PHB into flexible, thin films is one of the main factors that prevent its widespread application. Its high melting

[5] This film won the 11th Global Bioplastics Award, 2016 for a chocolate bar wrapper developed for Mars and Snickers bars packaging.

temperature (about 175−180°C) and low degradation temperature (220°C) limit the possibility of thermal processing to prepare PHB films. Approaches, such as heat treatment, copolymerization, blending (e.g., with PBAT) and the addition of plasticizers have been used to improve thermal processability and toughness. By using a combination of approaches mentioned above, PHB can be extruded, rolled or pressed into films having reasonably good mechanical properties (2016, **US2016230039** A1, UNIV ALBERTA).

Another PHA is PHBV (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)), that is less stiff and tougher, and it may be used as packaging material. Processability, impact strength, and flexibility can be improved, for example, by increasing the valerate content in a PHB copolymer.

3.7 Polyamides

Polyamides are used for the production of flexible plastic packaging due to their unique combination of properties:

- good barrier properties to oxygen, chemicals, and aroma substances;
- high mechanical strength (strength, stiffness, puncture resistance);
- high toughness;
- high heat distortion temperature;
- high transparency; and
- good thermoformability.

Polyamides can be processed as cast (CPA) and blown films and can be used for extrusion coating, and the production of biaxially oriented (BOPA) films. BOPA may be produced by both blown film process ("double bubble") and cast film ("tenter frame") process with simultaneous or sequential orientation. CPA is used mostly for thermoformable packaging applications. BOPA film can be used for a wide variety of applications, especially where high gas barrier properties are required [39]. BOPA films have excellent barrier to gas, fat, and transmission of aroma, exceptional mechanical strength and also high resistance to impact, puncture, and pin holing.

The most commonly used polyamides for the production of flexible plastic packaging are poly(ε-caprolactam) (nynlon 6) and poly(hexamethylene adipamide) (nylon 66), especially nylon 6/66 [39]. Nylon 66 has much higher melting temperature, thus better temperature resistance, but the nylon 6 is easier to process, and it is cheaper. These types of nylon have good oxygen and aroma barrier properties, but they are poor barriers to water vapor. Another interesting polyamide to be used as a packaging material is poly(metaxylylene adipamide) (nylon-MXD6).

The majority of polyamide films are mostly used as component layers of coextruded or laminated multilayer films for packaging of oxygen-sensitive food, such as meat and processed meat (sausage, bacon), cheese, dairy products, smoked fish, cereals, and semi-cooked meals.

3.7.1 Polyamide 6

Polyamide 6 (or nylon 6 or PA6), synthesized by ring opening of ε-caprolactam (see Fig. 3.1), is considered the ideal component for packaging with the best combination of barrier properties as well as mechanical strength. It is used for the packaging of high-value food products, including meat, cheese, pasta, and convenience food [39]. However, the majority of such applications combine nylon 6 with commodity plastics (mainly polyethylene) in multilayer films to make up for nylon's poor moisture barriers [40].

The recycling of multilayer films containing nylon 6 is problematic [8,40]. Nylon 6 is a tough material that becomes fluffy when shredded. It also has a high melting temperature, 220°C, which means it will often create lumps in the recyclate if the melting temperature of other materials is lower [8].

Representative examples of commercial nylon 6 products that are suitable for flexible plastic packaging are Ultramid B (BASF) and Akulon 6 (DSM).

Ultramid® B is an all-purpose nylon 6 (m.pt 220°C), which can be used as gas and aroma barrier in flexible plastic packaging, for example in sausage skins. BASF's Ultramid® B grades are processed into biaxially

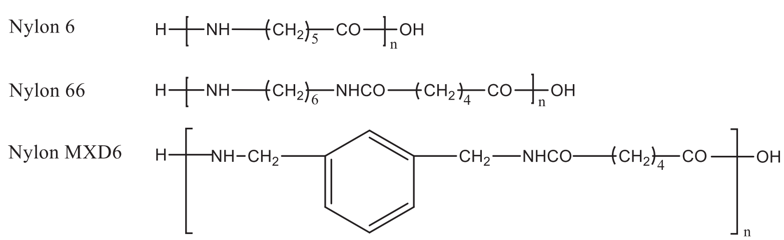

Figure 3.1 Chemical formulas of nylon 6, nylon 66, and nylon MXD6.

oriented (BOPA) and/or coextruded films for laminates/nonlaminates or thermoforming films. In high barrier EVOH-based structures, layers of Ultramid® film grades support and protect the EVOH, and thus, enhance its barrier performance [41].

Akulon® 6 (DSM) is a nylon 6 (m.pt 220°C), which has high-range processing (high-temperature resistance and high-viscosity extrusion grade), superior mechanical attributes, viscosity, low gel count, and ability to preserve moisture. It is used as a flexible barrier film in food packaging, protecting both fresh and processed food from spoilage aging and discoloration, as well as medical and industrial packaging [42].

Akulon® XS[6] (DMS) is a new type of nylon 6, which crystallizes much slower in the film bubble than conventional polyamide 6—matching the crystallization rate of other material layers. This creates a more stable bubble and extends the processing window, with no need to augment production with expensive, amorphous polyamides or polyamide copolymers. Importantly, the look and feel of Akulon® XS manufactured film are comparable to traditional film-grade polymers, despite being made from larger crystals. In fact, all its properties are the same [42].

3.7.2 Polyamide 66

Polyamide 66 (or nylon 66 or PA66), synthesized by step-growth polymerization of hexamethylene diamine and adipic acid (see Fig. 3.1), is quite similar to nylon 6, but it has slightly different characteristics. Nylon 66 has higher mechanical strength, stiffness, heat and wear resistance than nylon 6. It also has a better creep resistance, but lower impact strength and is approved for food contact. Nylon 66 benefits over nylon 6 extruded: Higher temperature rating, lower impact strength, and mechanical damping. Higher wear resistance and easier to machine. Representative examples of commercial nylon 66 materials that are suitable for flexible plastic packaging are Akulon® 66 (DSM) and Ultramid® A (BASF) (melting point, m.pt, 260°C).

Nylon 6/66 (PA6/66) is a copolyamide made from nylon 6 and nylon 66 (m.pt 190−195°C). Nylon 6/66 is suitable for film applications due to their good balance of properties, including easy processing, flexibility, strength, good optics, and barrier properties. A representative example of commercial nylon 6/66 is Ultramid® C37LC (BASF) [41]. However, the supply chain for nylon 66 and nylon 6/66 is under extreme, long-term

[6] Frost & Sullivan's 2016 European Barrier Films in Flexible Packaging Product Leadership Award.

pressure due to a lack of the key raw material 66 salt. Since the global supply of 66 salt is in shortage, it is placing pressure on the pricing and availability of both nylon 66 and nylon 6/66. A good alternative for nylon 6/66 is DSM's Akulon® XS [43].

3.7.3 Nylon-MXD6

Poly(m-xylylene adipamide) (nylon-MXD6) is a crystalline polyamide produced by Mitsubishi Gas Chemical Co., Ind. (see Fig. 3.1). A suitable grade of nynlon-MXD6 for the production of monolayers or multilayer films is S6007 of Mitsubishi [44].

Compared to nylon 6, nylon-MXD6 has the following favorable characteristics:

- greater tensile strength and tensile modulus of elasticity (Table 3.2);
- high T_g;
- low water absorption and moisture permeability;
- favorable crystallization speed and ease of molding and fabrication; and
- excellent gas-barrier properties against oxygen and carbon dioxide.

These features lead to greatly varied applications for nylon-MXD6 as a packaging material. Under certain conditions, its gas-barrier quality exceeds that of EVOH, PVDC, and polyacrylonitrile.

3.8 Polysaccharides

Polysaccharides are known for their complex structure and functional diversity. Film-forming polysaccharides include cellulose, starch (native and modified), dextran, pectins, seaweed extracts (alginates, carrageenan, agar), gums (acacia, tragacanth, guar), pullulan, and chitin/chitosan The linear structure present in cellulose (1,4-b-D-glucan), amylose (a component of starch 1,4-α-D-glucan), and chitosan (1,4-b-D-carbohydrate polymer) provide the films with hardness, flexibility, and transparency; the films are also resistant to fats and oils (2013, **WO2013042083** A1, UNIV DEL CAUCA; CT REGIONAL DE PRODUCTIVIDAD E INNOVACION DEL CAUCA CREPIC). Polysaccharide-based films usually show poor moisture barrier properties, but selective permeability to O_2 and CO_2 and resistance to oils [46,47]. The interest for films from polysaccharides

Table 3.2 Properties of Biaxially Oriented Film of nylon-MXD6 Versus nylon 6 and PET [45].

Property		Measuring Method ASTM	Nylon-MXD6	Nylon 6	PET
Thickness (μm)			15	15	15
Specific gravity			1.22	1.14	1.38
Haze			3.1	2.0	2.5
Tensile strength (MPa [kgf/mm^2])	MD	D882	220(22)	200(20)	160(16)
	TD		220(20)	220(20)	190(19)
Tensile elongation (%)	MD	D882	75	90	140
	TD		76	90	60
Tensile modulus (GPa [kgf/mm^2])	MD	D882	3.8(385)	1.7(170)	3.4(350)
	TD		3.8(390)	1.5(150)	3.9(400)
Impact strength (J kgf·cm)		D781	0.5(5)	1.0(10)	0.4(4)
Water vapor permeability (g/m^2·24 h)		JIS-Z0208 (B)	41	260	40

Nylon-MXD6 films: stretch ratio of nylon-MXD6: 4 × 4.

has grown in recent years because of their edibility, low permeability to oxygen, and contribution to quality preservation.

3.8.1 Cellulose and its Derivatives

Cellulose was one of the first materials to be used in packaging. Cellulose derivatives, i.e., cellulose functionalized in a solvent state with various side groups, are an important source of biopolymers for food packaging. Cellophane, methylcellulose, and carboxymethylcellulose are the three traditional film-forming cellulose derivatives in flexible food packaging. The most commonly used cellulose-based food packaging film is cellophane, a versatile thin transparent film made from plant cellulose [48]. The trademark "cellophane" is owned by Futamura (JP), which is the leading producer of cellophane packaging films worldwide.

Cellophane offers inherent benefits, such as excellent transparency and clarity in a broad range of colors, high gloss, heat resistance, naturally antistatic, and excellent dead-fold. It is used in food packaging, particularly when high stiffness is preferred to allow bags to stand upright. It is also used for nonfood applications where easy tearing is needed (see also Chapter 10; Section 10.2.4, Table 10.2). Several grades of cellophane are available in various formats, including:

- uncoated;
- vinyl chloride/vinyl acetate copolymer coated (semipermeable);
- nitrocellulose coated (semipermeable); and
- PVDC coated (good barrier, but not fully biodegradable).

Cellophane finds applications in specialty markets, including twist-wrapped confectionery, "breathable" packaging for baked goods, "live" yeast and cheese products and CelloTherm™ ovenable and microwaveable packaging [49]. Although cellophane is biodegradable, the way in which it is made results in a lot of other kinds of pollution. The last years, cellophane has been replaced by polypropylene in food packaging, mainly because of its poor performance at low temperature, limited shelf life, and high cost.

A range of cellulose-based packaging films is NatureFlex™, developed by Futamura [50]. The NatureFlex™ film types are available as uncoated, semipermeable, barrier and metalized films, and as labels for food packaging applications.

3.8.2 Starch

Starch is one of the most abundant, inexpensive, and commonly used natural polysaccharides. In its granular form, starch is normally a mixture of amylose and amylopectin polymers. Most starches, such as those from wheat, corn, and potato, contain about 25% amylose and 75% amylopectin. A high-amylose (>25%–75%) starch (from high-amylose rice, corn or peas) is a very useful film-forming material because it normally improves tensile strength, flexibility, and gas barrier properties [51]; see also **WO2008003165** A1 (2008, UNIV MANITOBA). A starch-based film is produced from thermoplastic starch (TPS), which is obtained by mixing starch with water or plasticizer (glycerol, sorbitol) under shear at an elevated temperature.

Starch is used in the formulation of biodegradable, edible films for the packaging of food (2008, **WO2008003165** A1, UNIV MANITOBA). Different starch formulations may lead to the formation of edible films with particular characteristics and properties. Among starches, cassava, corn, and wheat starches have been proposed for the formulation of edible films thanks to their availability and relatively low price [52].

Starch is blended with biodegradable polymers to improve its water resistance, processing properties, and mechanical properties. Typically, the starch content of these starch-based blends is lower than 50% [34] (see also Section 3.6.1.3). The starch-based grades of Mater-Bi® of Novamont containing various amounts of biodegradable polymers find applications in food packaging (e.g., bags, pouches, sealing films, cling film, or shopping bags) and cosmetic overwrap. The starch-based grades of Bioplast of Biotec contain potato-starch and other biologically sourced polymers. Bioplast film grades are suitable for blown-film extrusion applications, especially ultra-lightweight films with a thickness of about 10 µm, and are used as bags, fruit and vegetable bags, films and mailing films [53].

3.8.3 Chitin/Chitosan

Chitin is the second most common biopolymer and can be found in the exoskeleton of crustaceans, such as the shells of shrimps, and mollusks, but also in insects and fungi. It is in ample supply from by-products of the shellfish food industry. A film was made from chitin and cellulose that has the potential to replace flexible plastic packaging. The chitin is derived from crab shells, and the cellulose is derived from tree fibers. A large-scale manufacturing process has to be developed to make the new film competitive with the plastic film on cost. While there are plenty of industrial processes available to produce cellulose, methods to produce chitin are still developing [54].

Chitosan is a polysaccharide derived by the alkaline deacetylation of chitin. It has great potential for applications in food technology, owing to its biocompatibility, nontoxicity, short time biodegradability, and excellent film-forming ability. Chitosan also has inherent antimicrobial, antifungal, and barrier properties. Further, it has the ability to form edible films that can carry and release compounds with antimicrobial or antioxidant abilities [46,55–57]. Chitosan could also be used as a sensing film in food packaging to detect the quality of the food. It can be combined with other biomaterials to develop sensing films, which could be sensitive to pH, microbial enzyme, and microbial metabolism [57].

3.9 Blends of Polymers

A polymer blend is a mixture of at least two polymers having different physical properties than the constituting polymers. A polymer blend forms either a single phase (with a single T_g), and is called *miscible*, or multiple phases (with at least 2 T_gs), and is called *immiscible*. The vast majority of polymer blends are immiscible. In practice, the term compatibility is used instead, which describes the degree to which polymers interact. Compatibility creates a disperse phase with size and stability determined by interfacial interactions. A compatible polymer blend is an immiscible blend that exhibits macroscopically uniform physical properties. Miscibility is of maximum compatibility. However, compatibility is a relative term and is not well defined. The compatibility of two polymers is better when their solubility parameters (see Table 3.3) are close to each other depending on their interaction strength (e.g., presence of hydrogen bonding and polar interactions) [58].

Most polymers used in flexible multilayer plastic packaging are incompatible as can be seen in Table 3.4. Even chemically similar polymers like polyethylene and polypropylene are incompatible to each other. The provided compatibility indicators are purely indicative. Commercial packaging films contain specific polymer grades and additives which affect the compatibility of the polymers constituting the blend. Polymers, even in the same family, may not readily mix if their densities are substantially different [62].

A compatible blend is PLA/PBAT, the biodegradable plastic Ecovio® (BASF) made from PLA and Ecoflex® (BASF) (see Section 3.6.1.3). Its first application area is in flexible packaging films, e.g., for the production of shopping bags.

Table 3.3 Average Solubility Parameter (δ_h) of Selected Polymers Used in Flexible Multilayer Packaging [58–61].

Polymer	**δ_h (MPa$^{1/2}$)**
PE (LDPE, LLDPE, HDPE)	16.4–16.7
PP	16.2–16.6
PVC	19.5–19.6
PVDC	18.9–21.3
PET	20.5–21.2
PA6	25.5–26.0
PA66	26.0–28.0
PVOH	30.5
EVOH (32 mol%)	38.9

EVOH, *ethylene-vinyl alcohol;* HDPE, *high density polyethylene;* LDPE, *low- density polyethylene;* LLDPE, *linear low- density polyethylene;* PA6, *polyamide 6;* PA66, *polyamide 66;* PE, *polyethylene;* PET, *poly(ethylene terephthalate);* PP, *polypropylene;* PVC, *poly(vinyl chloride);* PVDC, *poly(vinylidene chloride);* PVOH, *poly(vinyl alcohol).*

The major problem in the recycling of used flexible multilayer plastic packaging is connected to a great inhomogeneity of the polymers present in the waste. The eventual incompatibility of the different layers is the most important reason of the difficult processing and inferior mechanical properties of the resulting products from mixed, chemically different polymers If the waste stream includes incompatible polymers, such as in a multilayer structure, the incompatible portion will move to the outside of the extrudate and result in die build-up.

One possible solution is the use of compatibilizers. Theses additives are responsible for enhancing the phase dispersion and stability; especially, polymer compatibilizers have shown to be a useful tool for the recycling of multilayer packaging based on incompatible polymers (e.g., polyethylene, PET and nylon). However, despite of presenting good physico-mechanical properties, care must be taken when analyzing the viability of recycling the compatibilized film waste from an economic perspective. The use of higher amounts of compatibilizer (as in the case of 10 or 15 w%) is not a common practice among the recycling industry, due to the high costs of the compatibilizers [63]; see also Chapter 8, Section 8.7.1.1.

Table 3.4 Compatibility of Commonly Used Polymers in Flexible Packaging

Polymer	PE				PP	PVC	PET	PA6, PA66	PVDC	EVOH
		LDPE	LLDPE	HDPE						
PE	M	M	M	M	*	*	*	*	*	*
LDPE	M	M	M	M	*	*	*	*	*	*
LLDPE	M	M	M	M	*	*	*	*	*	*
HDPE	M	M	M	M	*	*	*	*	*	*
PP	*	*	*	*	M	*	*	*	*	*
PVC	*	*	*	*	*	M	*	*	**	*
PET	*	*	*	*	*	*	M	*	*	*
PA (PA6, PA66)	*	*	*	*	*	*	**	M	*	**
PVDC	*	*	*	*	*	**	*	*	M	*
EVOH	*	*	*	*	*	*	*	**	*	M

, incompatible; **, semi-compatible; *, compatible.* M, *miscible different grades.*
Adjusted from Merrington A. Recycling of plastics. In: Kutz M, editor. Applied plastics engineering handbook. Elsevier; 2017. p. 167–189.

3.10 Polymers Used as Adhesives and Tie Layers

Tie layers are special adhesives that are used to bond the incompatible layers of a flexible multilayer plastic packaging, mainly in coextrusion. The vast majority of the polymers used in coextrusion as tie layers are maleic anhydride grafted polyolefins, such as Byne®l (Dow, ex Dupont), Admer™ (Mitsui), and Orevac® (Arkema).

Adhesives are also used to attach labels and closure systems on flexible plastic packaging.

Most commonly used polymers as adhesives for flexible food packaging are polyurethane and acrylics. Solvent-based polyurethane adhesives are used for dry bond lamination (e.g., HI-THANE™ of Singwon); polyurethane aqueous dispersions are used for wet-bond adhesion (e.g., Epotal® P 100 ECO and Epotal® FLX 3621 of BASF); see also Chapter 4, Section 4.1.2.

Some of the main players in global flexible packaging laminating adhesives market include 3M, Henkel, H.B. Fuller, Dural Industries, Bond Tech Industries, and DIC Corporation [64].

Stripping agents are used for the dissolution or swelling of the tie layers and separation of the individual layers from a multilayer packaging film (see Chapter 7, Section 7.1).

3.11 Polymers Used as Coatings/Sealants

Coatings are applied to the inside or outside (e.g., food contact layer), outside (e.g., nonfood contact layer) or in between layers to either alter the physical properties or enhance the aesthetics of the packaging. The various types of coating include protective coatings, primers, sealants, release coatings, gas barriers, antimist coatings, etc. Many applications in the area of flexible packaging require the use of a primer. The primer task of a primer is to enable the adhesion of layers (e.g., inks, adhesives, other film types). The various types of coatings used in flexible multilayer plastic food packaging are shown in Table 3.5.

Representative combinations of layers and coatings used in the manufacture of flexible multilayer plastic packaging are shown in Table 3.6.

A typical beverage flexible package has the structure: PET/print/primer coating/LDPE/foil/LDPE (heat seal). A typical retort flexible package has the structure: PET/print/primer coating/LDPE/foil/LDPE (heat seal). The

Table 3.5 Coatings Used in Flexible Multilayer Plastic Food Packaging

Coating Material	Type of Coating	Function
Nitrocellulose, reactive polyurethane systems, ionomers (e.g., Surlyn® of Dow [ex DuPont])	Protective coating	Protects the surface from mechanical damage
Polyacrylate dispersion (e.g., Epotal® A 816 of BASF); polyester-polyurethane dispersion (Luphen® 700 of BASF)	Top coatings	Top coat for polymeric film
EEA, EAA, EVA, PVDC, ionomers[a]	Heat sealable coating	Allow heat sealability for nonsealable materials
Water-based acrylate dispersion (e.g., Aquatack®, 1422 of Paramelt); water-based polyurethane (e.g., Emuldur® 381 A, Epotal® P 350 and Luphen® 700 of BASF; Aquatack®, 1411 & 1467 of Paramelt)	Primer	Improves the bond between a polyolefin film and an otherwise incompatible coating
Blends of acrylic resins and latex; synthetic rubber	Cold sealable coating	Coatings that can be sealed self-to-self using just pressure (e.g., for flow-wrapping heat-sensitive products like chocolate or ice cream)
Polyamide (Nylon)	Release lacquers	Applied to the opposite surface of a plastic film that is

Table 3.5 Coatings Used in Flexible Multilayer Plastic Food Packaging (*Continued*)

Coating Material	Type of Coating	Function
		coated with cold seal to prevent sticking and to promote easy unwinding from the reel
PVDC	Antimist	Prevents formation of condensate droplets/ fogging on the food contact side (e.g., in fresh salad packaging)
PVDC, AlO_x vapor coating	Gas barrier	Barrier to oxygen/ moisture/odors/ flavors

EAA, *ethylene-acrylic acid;* EEA, *ethylene-ethyl acrylate;* EVA, *ethylene-vinyl acetate;* PVDC, *poly(vinylidene chloride).*

[a]*EAA or EMA neutralized with cations (e.g., Na^+, Zn^{2+}, Li^+).*

Adjusted from Mieth A, Hoekstra E, Simoneau C. Guidance for the identification of polymers in multilayer films used in food contact materials: user guide of selected practices to determine the nature of layers; EUR 27816 EN. Joint Research Centre (JRC) Technical Report, JRC100835. European Commission; 2016. https://doi.org/10.2788/10593.

Table 3.6 Substrates and Coatings Used in Flexible Plastic Packaging [66].

Layer	Coating
PET	Primers
Polyethylene	Adhesive coating
OPP/BOPP	Wash coats
CPP	PVOH
Nylon	Lacquers
MetPET	Varnishes
Cellophane	Acrylic polyurethanes
Aluminum foil	PVDC

BOPP, *biaxially oriented polypropylene;* CPP, *cast polypropylene;* MetPET, *metalized PET;* OPP, *oriented polypropylene;* PET, *poly(ethylene terephthalate);* PVDC, *poly(vinylidene chloride);* PVOH, *poly(vinyl alcohol).*

foil is a barrier layer and may be substituted with metalized PET, nylon of EVOH depending on the type of barrier required.

Sealant layers provide low-temperature sealability for fast packing line speeds and may also contribute to barrier performance. EVA, EEA, LDPE, LLDPE, polyethylene plastomers, and ionomers are standardly used, among which ionomers additionally provide exceptional oil and grease resistance [26,67]. Metallocene catalyzed polyethylene provides better fast-tack than EVA without the odor and taste transfer associated with EVA [68].

3.12 Polymers Used as Inks

Many different types of resins are used in the ink formulations for printing on flexible packaging, including styrene, acrylics (e.g., Joncryl® acrylics of BASF), polyurethanes (e.g., Versamid® PUR of BASF) e.g., polyamides (e.g., Versamid® 970 series of BASF), nitrocellulose, etc. The use of nitrocellulose is not recommended in retort packaging due to the formation of nitrosamines caused by the exposure of it in the packaging to high temperatures. Polyurethane resins create a flexible film and provide superior lamination bond strengths that prevent delamination of the packaging; they are not as effective as other resins when it comes to pigment dispersion and also tend to be harder to print with. For this reason, polyurethanes tend to require a coresin to help improve the pigment dispersion [69].

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Patents

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EP0374783 A2	19900627	AU4685289 A 19900621; AU634991 B2 19930311; CA2003882 A1 19900619; CA2003882 C 19970107; DE68903478 T2 19930408; EP0374783 A3 19900919; EP0374783 B1 19921111; JPH02229835 A 19900912; JPH02229835 A 19900912; jP2573527 B2 19970122; jP2573527 B2 19970122; US5434010 A 19950718; US6100357 A 20000808; US6197909 B1 20010306	US19880286019 19881219	SMITH ERWIN ROGERS; SCHUETZ JEFFREY MICHAEL; LUSTIG STANLEY	VISKASE CORP	Heat shrinkable very low-density polyethylene terpolymer film.
EP0870802 A1	19981014		EP19970105841 19970409	DEWART JEAN-CHRISTOPHE; EVERAERT JACQUES	FINA RESEARCH	Medium density polyethylene compositions for film applications.
EP3144349 A1	20170322	EP3144349 A4 20180110; EP3144349 B1 20190213; CN106459548 A 20170222; JPWO2015174396 A1 20170420; JP5933852 B2 20160615; US2017267851 A1 20170921; US10053566 B2 20180821; WO2015174396 A1 20151119	JP20140098431 20140512; WO2015JP63587 20150512	YAMAKOSHI SATOSHI; KAWAKAMI NAOKI	KURARAY CO	Ethylene-vinyl alcohol composition pellets.

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Patent Number	Publication Date	Family Member	Priority Number	Inventor	Applicant	Title
EP3398768 A1	20181107	AU2016381909 A1 20180712; CN108472928 A 20180831; JPWO2017115736 A1 20181018; KR20180098557 A 20180904; TW201736140 A 20171016; WO2017115736 A1 20170706	JP20150257295 20151228; WO2016JP88617 20161226	INAGAKI JUN; NUMATA YUKIHIRO; VAN BERKEL JESPER GABRIËL	TOYO BOSEKI; SYNVINA C V	Laminated polyester film.
US2007120283 A1	20070531	CA2626650 A1 20070705; WO2007076165 A2 20070705; WO2007076165 A3 20080110	US20060550611 20061018; US20050727726P 20051018	HOSTETTER BARRY J; WELCH PHILIP F	APPLIED EXTRUSION TECHNOLOGIES	Polypropylene films emplying recycled commercially used polypropylene based films and labels.
US2008233413 A1	20080925		US20080105343 20080418; US20060550611 20061018; US20050727726P 20051018	HOSTETTER BARRY JASON; WELCH PHILIP F	APPLIED EXTRUSION TECHNOLOGIES	Polypropylene films emplying recycled commercially used polypropylene based films and labels.
US2016230039 A1	20160811	CA2920431 A1 20160810	US201615040579 20160210	ELIAS ANASTASIA; ANBUKARASU PREETAM; SAUVAGEAU DOMINIC	UNIV ALBERTA	Polyhydroxy-alkanoate film formation using alkanoic acids.
US5286424 A	19940215	CA2102676 A1 19940510	US19920973858 19921109	SU TIEN-KUEI; LILLY JR KENNETH L	MOBIL OIL CORP	Recycling polyolefins coated with chlorine-containing polymer.
US6114456 A		US6114456 X6 20000905	EP19970105841 19970409; US19970977723 19971125; US19970034900P 19970207; EP19960118843 19961125	DEWART JEAN-CHRISTOPHE; EVERAERT JACQUES	FINA RESEARCH	Medium density polyethylene compositions for film applications.

WO2008003165 A1	20080110	CA2552179 A1 20080106; CA2656293 A1 20080110	CA20062552179 20060706	HAN JUNG	UNIV MANITOBA	Physical and mechanical properties of pea starch edible films containing beeswax emulsions.
WO2009019277 A1	20090212	CN101772541 A 20100707; EP2022824 A1 20090211; EP2176340 A1 20100421; EP2471857 A1 20120704; RU2443729 C2 20120227; RU2443729 C2 20120227; US2010249329 A1 20100930 US8173747 B2 20120508	EP20070114025 20070808	GREIN CHRISTELLE; SCHEDENIG TONJA	BOREALIS TECH OY	Sterilisable and tough impact polypropylene composition.
WO2013042083 A1	20130328	CO6350195 A1 20111220; US2014230690 A1 20140821; US2014235763 A1 20140821; US9109116 B2 20150818; US9416275 B2 20160816; WO2013042094 A1 20130328	CO20110124719 20110923	VILLADA CASTILLO HECTOR SAMUE; NAVIA PORRAS DIANA PAOLA; CASTANEDA NINO JUAN PABLO	UNIV DEL CAUCA; CT REGIONAL DE PRODUCTIVIDAD E INNOVACION DEL CAUCA CREPIC	Biodegradable packaging obtained from cassava flour and fique fiber and their manufacture process.
WO2014158316 A1	20141002	CA2900848 A1 20141002; CN105189075 A 20151223; CN105189075 B 20171031; EP2969443 A1 20160120; EP2969443 A4 20161019; EP2969443 B1 20180221; HK1220665 A1 20170512; JP2016522099 A 20160728; MX2015011162 A 20151111; US2014048631 A1 20140220; US2015375425 A1 20151231; US2016236377 A1 20160818; US2018065276 A1 20180308; US9120104 B2 20150901; US9138749 B2 20150922; US9346192 B2 20160524	US201313796143 20130312; US201314063045 20131025	KULESA ROBERT FRANCIS; FEENEY JAMES J; CARLSTEDT RICHARD WAYNE; BLAKE DANIEL WILLIAM; HACKER BUCKELL GARY; JOHNSON ABBY MARIE	WISCONSIN FILM & BAG INC	Post-consumer scrap film recycling process and system.

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Patent Number	Publication Date	Family Member	Priority Number	Inventor	Applicant	Title
WO2016027194 A1	20160225	BR112017003303 A2 20171128; CA2956349 A1 20160225; CN107075023 A 20170818; EP3183277 A1 20170628; JP2017525812 A 20170907; KR20170046151 A 20170428; MX2017001711 A 20170427; TW201609827 A 20160316; TWI617588 B 20180311; US10189922 B2 20190129; US2017226244 A1 20170810	US201462038965P 20140819	GOYAL SHIVENDRA; GILLON BRONWYN; DOBBIN CHRISTOPHER; SALOMONS STEPHEN	NOVA CHEM INT SA	Very low density polyethylene produced with single site catalyst.
WO2016032330 A1	20160303	AU2015307312 A1 20170413; CN106715546 A 20170524; EP3186064 A1 20170705; JP2017527684 A 20170921; KR20170045305 A 20170426; US2017297256 A1 20171019	NL20142013360 20140825; US201462041309P 20140825	KOLSTAD JEFFREY JOHN; VAN BERKEL JESPER GABRIËL	FURANIX TECHNOLOGIES BV	Process for producing an oriented film comprising poly(ethylene-2,5-furandicarboxylate).