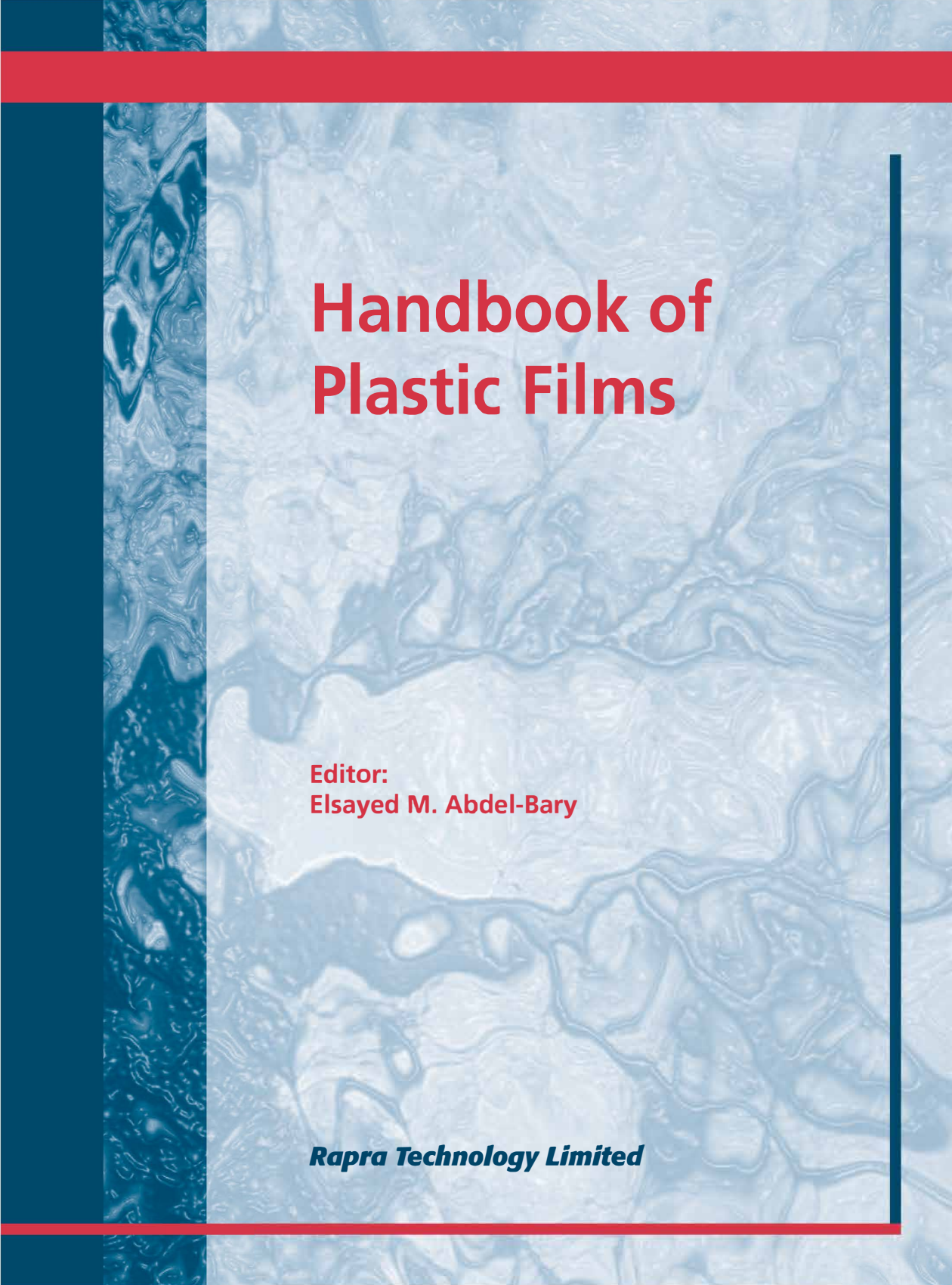


The cover features a light blue background with a subtle, swirling pattern. A dark blue vertical band runs along the left edge, and a red horizontal band runs across the top. The title is in a large, bold, red font. The editor's name is in a smaller, bold, red font. The publisher's name is in a bold, dark blue font.

Handbook of Plastic Films

Editor:
Elsayed M. Abdel-Bary

Rapra Technology Limited

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Editor: E.M. Abdel-Bary



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1 Technology of Polyolefin Film Production

Robert Shanks

1.1 Introduction

A film is a two-dimensional form of a polymer. A film is typified by a large surface area to volume ratio. Films are required to exhibit barrier properties to any contaminating substances that may try to enter, or any desirable substances that may try to leave, across the film. This property is resistance to diffusion. Since a film is very thin, it must have high mechanical properties such as tensile strength, impact resistance and tear strength. The mechanical properties usually depend on molecular structure, molar mass and molar mass distribution. Visibility through a film is often important, so low haze will be required. These are the bulk properties of the film [1].

The film will often be required to improve the appearance of an item contained within it, so surface properties such as gloss and printability are important. The latter property, printability, is related to a relatively high surface energy to achieve wetting and good work of adhesion. Suitable surface energy may be achieved through modification. Protection may also be improved if the friction is low; this property is called slip. When a film is used to enclose and protect items, it may need to provide adhesion to itself or to the contents. The immediate form of adhesion is called tack. Subsequently the polymer must flow to provide complete adhesion.

Manufacture of a film will usually be through an extrusion of the melt, so the melt rheology must be suited to the manufacturing process. Rheology is controlled by chemical structure, molar mass and long branches. The way in which the film is extruded, extended and solidified by cooling will control the microstructure and hence many of the properties. A summary of the various polyolefins used in film manufacture is provided in **Table 1.1**.

In this chapter, polyolefin films are reviewed. First, the various types of polyolefins and their suitability for film manufacture are considered. The rheology, structure and properties of the polymers are discussed in relation to the type of film manufacturing processes that are most applicable to the types of polymer. Post-extrusion modifications of the films, such as orientation, surface chemistry and additives, are discussed. Characterisation methods used to measure film mechanical properties, structure and additives are described, as well as other more specific properties. Finally, some important particular applications that require special structures or modifications are described.

Table 1.1 Structure, properties and description of the polyolefins used for film production					
Polyolefin	Comonomer	Density	Preparation method	Mechanical properties	Comments
High-density or linear polyethylene (HDPE, LPE)	No branches	0.94-0.96	Zeigler-Natta	High tensile strength, low impact strength	Brittle film, with good gas barrier properties
Low-density polyethylene (LDPE)	Random short and long branches	0.91	Radical, with autoclave or tubular reactor	Non-Newtonian melt rheology, good impact strength	Good blown extrusion characteristics for flexible films
Linear low-density polyethylene (LLDPE)	1-Butene, 1-Hexene, 1-Octene	0.91-0.93	Zeigler-Natta	Intermediate strength with elasticity, melt rheology more Newtonian than LDPE	High-clarity, glossy film, difficult to extrude
Very-low-density polyethylene (VLDPE)	1-Butene, 1-Hexene, 1-Octene	0.89-0.91	Single-site metallocene	Tough elastic, moderate strength	High-clarity, very glossy film, very thin films possible
VLDPE with long branches	1-Butene, 1-Hexene, 1-Octene	0.89-0.91	Constrained geometry single site	Tough elastic, moderate strength, non-Newtonian melt rheology	Easy to process, improved melt strength
Ultra-low-density polyethylene (ULDPE), plastomers	1-Butene, 1-Hexene, 1-Octene	<0.89	Single-site metallocene	Elastic, low tensile strength, low modulus	Thermoplastic elastomer, narrow low temperature melting, good for heat seal
Polypropylene	No branches	0.90	Zeigler-Natta	High tensile strength, brittle, temperature resistance	Transparent, high-strength and temperature-resistant glossy films
Polypropylene copolymer with ethylene, block or random	Ethylene	0.90	Zeigler-Natta	Tough with high melting temperature (block) or softer with lower melting temperature (random)	Tough films, with more milky colour
Polypropylene and copolymers with ethylene	Ethylene	0.90	Single-site metallocene	Narrow molar mass distribution, random comonomer distribution and high isotacticity	Flexible, elastic transparent films

1.2 Structures of the Polyolefins

1.2.1 Low-Density Polyethylene (LDPE)

Molecular structures of some example polyethylenes are shown in **Figure 1.1**. LDPE has rheological properties that are suitable for production of film by the blown film process [2]. LDPE has some long branches and many short branches. Typically, there may be three long branches and 30 short branches per molecule. The molar mass is relatively low, and it has a broad molar mass distribution. The melt strength, or zero-shear viscosity, and the shear-thinning nature of LDPE enhance processing. The film has relatively low tensile strength but good impact strength. LDPE films show good clarity (i.e., low haze) and gloss. The good clarity and gloss result from relatively low crystallinity. LDPE is polymerised by the high-pressure radical process. There are two main reactor types, the autoclave and the tubular reactor. The autoclave tends to provide more branching and broader molar mass distribution. LDPE has a broad melting range, with a peak melting temperature of 110 °C. The density may vary from 0.915 to 0.930 g/cm³ for LDPE.

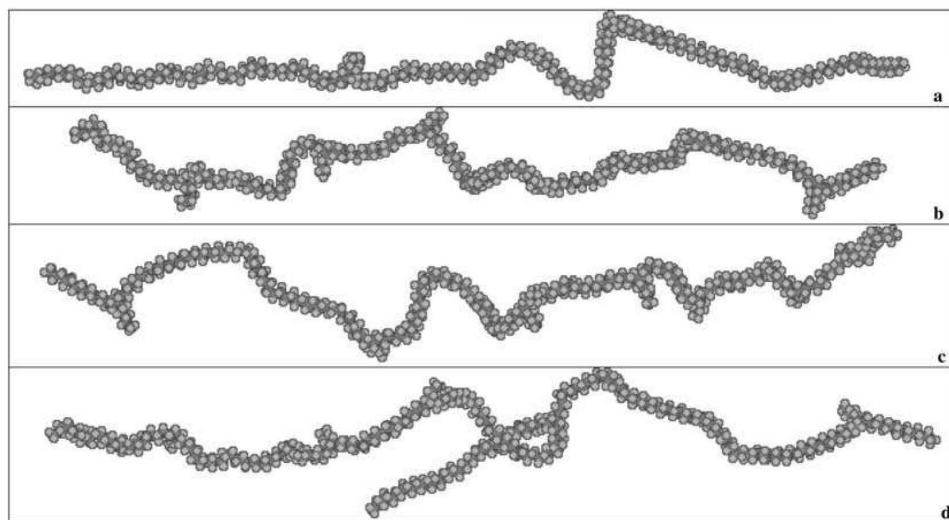


Figure 1.1 Molecular structures for linear and branched polyethylenes (LPE and BPE) with 100 monomers, four or eight short branches, and one long branch of 40 carbons: (a) LPE (100); (b) BPE (4, 100); (c) BPE (8, 100); and (d) BPE (8, L1(40), 100)

1.2.2 High-Density Polyethylene (HDPE, MDPE, UHMWPE)

HDPE has a linear structure, with little or no branching. HDPE is typically formed by the Ziegler-Natta, Phillips or Unipol processes. Each process involves relatively low pressure and is catalysed by an organometallic complex with a transition metal. Polymerisation is usually performed in slurry with a liquid such as heptane, or in the gas phase with the catalyst in a fluidised bed form. Variations of HDPE are ultra-high molar mass polyethylene (ultra-high molecular weight polyethylene, UHMWPE), where the molar mass is of the order of 1,000,000 g/mol, and medium-density polyethylene (MDPE), where some short branches are introduced by copolymerisation with a 1-alkene, such as 1-butene. HDPE has higher crystallinity and therefore shows higher tensile strength than LDPE, though its impact strength is deficient for many applications. UHMWPE provides increased tensile strength due to the longer molecules providing more tie molecules between crystals. MDPE provides better impact strength because of its reduced crystallinity. HDPE shows a more Newtonian rheology than LDPE, and so is less suitable for extrusion processing, by either the blown film or cast film processes [3].

1.2.3 Linear Low-Density Polyethylene (LLDPE)

LLDPE is a copolymer of ethylene and a 1-alkene, typically 1-butene, 1-hexene or 1-octene, though branched alkenes such as 4-methyl-1-pentene are also used. These polymers have densities in the range 0.915-0.930 g/cm³ and they contain 2-7% (w/w) or about 1-2% mol/mol of the 1-alkene. They are polymerised using multisite catalysts such as Ziegler-Natta with either a gas-phase or slurry process. Since the boiling temperature of 1-octene is too high for the gas-phase process, the slurry process must be used. The comonomer composition has a broad distribution, so that some molecules, or segments of molecules, have few branches while others have many branches. This distribution is reflected in the broad melting temperature range of the LLDPE. The properties of LLDPE tend to be in between those of LDPE and HDPE. They have short branches but not long branches, so that crystallisation-dependent mechanical properties are improved, but processing rheological properties are inferior to those of LDPE [4].

1.2.4 Very- and Ultra-Low-Density Polyethylene (VLDPE, ULDPE)

Very- (density 0.89-0.915 g/cm³) (VLDPE) and ultra- (density <0.89 g/cm³) (ULDPE) low-density polyethylenes have higher copolymer content. ULDPE are also called polyolefin elastomers (POE) because of their properties. These polyethylenes have recently been commercialised as a result of the new metallocene catalyst technology that allows higher comonomer levels and provides a narrower distribution of comonomer composition as

well as of molar mass. These polymers have lower melting temperatures, less crystallinity, greater toughness and elasticity, but lower tensile strength than other polyethylenes. They mainly only have short branches, but some varieties also have some long branches [5].

1.2.5 Polypropylene (PP)

Isotactic polypropylene (iPP) is useful for temperature-resistant and glossy film production. iPP has greater strength and higher melting temperature than any of the other polyolefins. The crystal size can be made small by rapid cooling and/or nucleating agents, so that highly transparent, high-gloss films can be produced. The rheological properties are not ideal for the blown film process, but such processing is used in a two-stage extrusion and blowing process. Syndiotactic PP (sPP) is now becoming available commercially as a result of metallocene catalyst polymerisations. sPP provides more elastic films than iPP. iPP has many advantages over polyethylenes because of its strength, thermal resistance, gloss and clarity. It is particularly suitable for more durable products [6].

1.2.6 Polypropylene Copolymers

Copolymers of propylene with small amounts of ethylene (0-5% w/w) provide increased toughness, at the expense of tensile strength. Random copolymers show the greatest property changes, such as increased elasticity and a decrease in melting temperature. Copolymers with more block-like structure, where the ethylene is distributed in some of the molecules or molecular segments, provide a good compromise in properties between toughness and strength.

1.3 Morphology of Polyolefin Films

All the polyolefins are semicrystalline polymers. The crystallinity provides the tensile strength but reduces the transparency. Larger crystals scatter transmitted light, producing an opalescent appearance, known as haze. Crystals on the surface reduce the surface smoothness and cause surface scattering of incident light and reduce the gloss. An example of the morphology of a polypropylene film is provided in the optical microscope picture in **Figure 1.2**. Processing conditions can modify the natural tendency of each polyolefin to provide these crystallisation-dependent properties. Rapid cooling will give smaller crystals. So the use of cold rollers in the cast film process usually gives smaller crystals and in particular greater surface smoothness. In the blown film process, the use of a refrigerated air stream increases the crystallisation rate. Crystallisation is evident as a fogging of the film a short distance from the extrusion die; this is called the frost-line height. Orientation can be measured using wide-angle X-ray scattering (WAXS) [7].

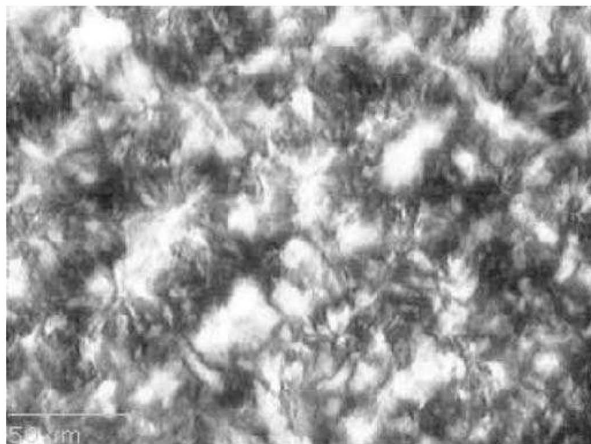


Figure 1.2 Polarised optical microscope picture of polypropylene blended with 30% poly(ethylene-co-propylene). The copolymer is a dispersed phase shown by the dark regions mainly at the edges of the polypropylene spherulites

Orientation of crystals will direct the axes of the crystals, and correspondingly the crystal-dependent properties, along the orientation or draw direction. Usually films are oriented, or drawn, in two orthogonal directions, called biaxial drawing, first parallel to the extrusion direction, then laterally. Drawing in the extrusion direction involves cooling the melt until crystallisation takes place, then passing the film between rollers with increasing differential speed. The lateral drawing depends on the method of manufacture. When the blown film process is used, orientation is provided during the blowing process. The cast film process requires a lateral drawing frame called a tenter. The edges of the film are grasped and the frame moves apart as the film moves forward. Orientation provides enhanced physical properties in the drawn directions. When the film is biaxially drawn, the properties are greater in the direction that was drawn last [8].

1.4 Rheological Characterisation of the Polyolefins

1.4.1 High-Density Polyethylene

HDPE consists of linear molecules. The shear stress versus shear rate curve will be approximately linear except for very high molar mass. The linear relationship is Newtonian. This means that at high shear rates, as experienced in processing, the viscosity

is high and so the force required for extrusion will be high. Another problem is that the viscosity at low shear rates is not increased. This zero-shear viscosity is related to the melt strength of the polymer. If the melt strength is low, the molten film may rupture as it emerges from the extruder as a tube that is then rapidly expanded by a gas pressure. High melt strength is required to resist rupture and create a dimensionally stable bubble. The melt strength is less critical in the cast film process, although the film must remain stable until it reaches the cooling rollers. The force required for extrusion will still be a problem, since more energy will be needed to extrude a particular mass of polymer, and this will require more electricity and a more powerful extruder motor. HDPE has high tensile strength, but low impact and tear strengths, so damage during processing by tearing is a potential problem. Processing of HDPE can be improved by blending with other polyethylenes, in particular LDPE.

1.4.2 Linear Low-Density Polyethylene

LLDPE typically have a broad molar mass distribution and a broad distribution of the 1-alkene comonomer, or branches. The tensile strength is lower than that of HDPE but higher than for LDPE. They have improved toughness compared with HDPE. Though they have short branching comparable with LDPE, they do not have long branches. The lack of long branches decreases their shear-thinning rheological characteristics compared with LDPE and so processing is not as efficient. They are often blended with LDPE since the long branches enhance processing. They have greater tensile strength than LDPE, but, with their higher crystallinity, they are less transparent.

1.4.3 Very- and Ultra-Low-Density Polyethylene

VLDPE and ULDPE have many short branches distributed along the main chains more evenly than for LLDPE where single-site catalysts have been used in the polymerisation. Short branches are not important in the rheology. These polymers will have essentially Newtonian behaviour. Polymers with very high molar mass have more pronounced shear thinning, though entanglements between only the main chains are not as effective as between several long chains such as when long branches are present.

1.4.4 Low-Density Polyethylene, Long Branches

LDPE has long branches that are known to provide non-Newtonian rheological response. LDPE is shear thinning, so that the power required for extrusion at typical high shear rates is less than proportional to the shear rate. This makes extrusion of LDPE more

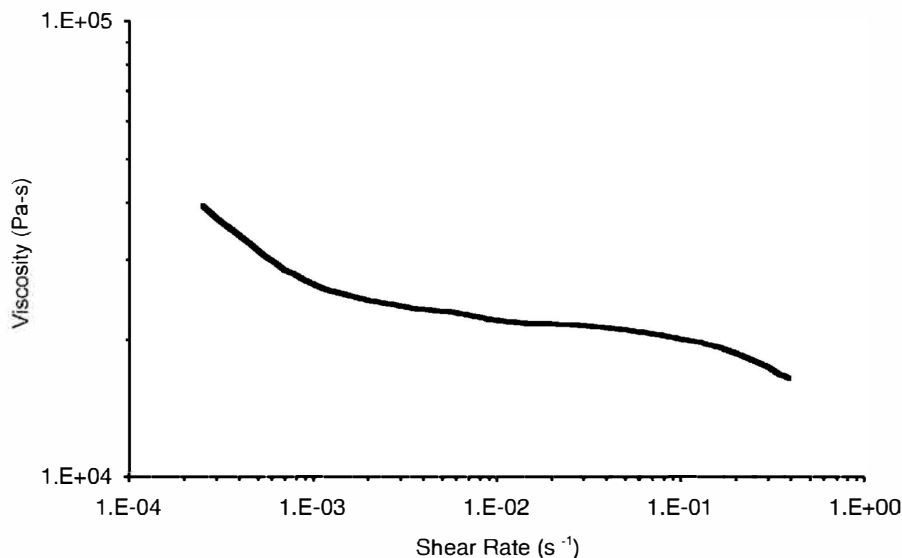


Figure 1.3 Parallel plate, continuous shear rheology curve for low-density polyethylene at 200 °C

economical than for other polyethylenes, and the extruder motor does not need to be as powerful. At low shear rates, the viscosity rises significantly, so the zero-shear viscosity, or melt strength, is high. A typical rheology curve for LDPE is shown in Figure 1.3. LDPE has better bubble strength in the blown film process, so that resistance to bursting and bubble stability are greater prior to solidification. In the cast film process, the film will be stable in the molten state between the extrusion die and the cold rollers. The long branches provide more intermolecular entanglements when the shear rate is low. As the shear rate increases, the long branches break free of entanglements and the viscosity decreases markedly. These rheological characteristics are of prime importance during processing [9].

1.4.5 Polypropylene

Polypropylene has a methyl branch on each monomer unit and so a pseudo-asymmetric carbon is present. This introduces tacticity, and the isotactic form of polypropylene is the only one that is suitable for film formation. Polymerisation is performed using Ziegler-Natta and several other newer proprietary catalysts. The catalysts have been developed

to provide maximum isotactic structure (>99%), so that atactic polypropylene does not need to be extracted and the mechanical properties are maximised. High catalytic activity is desired so that residual catalyst does not need to be extracted from the polymer.

Polypropylene has a lower density than most of the polyethylenes (0.905 g/cm³) and a higher strength. Its melting temperature at 162 °C is significantly higher than that of HDPE, making it suitable to form retortable and microwave-resistant products. The glass transition temperature is high, (e.g., 10 °C, but this varies with the crystallinity and method of measurement) so impact resistance is poor. Impact resistance is improved by copolymerisation with ethylene. Usually about 5% ethylene is used, and blocky copolymers are formed, so that the ethylene-containing molecules form an immiscible dispersed phase in a matrix of homopolymer polypropylene. The toughness is increased without decreasing the overall melting temperature significantly. Other random copolymers provide increased toughness and elasticity with decrease in tensile strength and melting temperature.

Single-site or metallocene-catalysed polypropylenes have narrower molar mass distribution, though the isotacticity may not be greater. The copolymers with ethylene have a more even distribution of ethylene, and so a very small proportion of ethylene will provide a large decrease in melting temperature compared with the traditional polypropylene copolymers.

1.5 Blown Film Production (Tubular Extrusion)

Formation of film is by extrusion. The extrusion process involves a series of events that each affect the stability and consistency of the extrudate and hence the film. The processes in the extruder include feed, melting, mixing, metering and filtration. The die is an annular shape that produces a tube of polymer. The tube is inflated by air pressure injected inside at the die. Inflation of the tube makes the film dimensions greater and provides orientation of the polymer. The tube passes through zones of cooled air, which solidifies the polymer and controls the crystallisation [10]. A diagram showing the essential features of the blown film process is shown in **Figure 1.4**.

In the formation of polypropylene, a two-step tubular orientation process is required. This is because of the poor melt strength of polypropylene. The film must first be cooled to enable crystallisation. The film is reheated to be just at the melting temperature and the tube is blown again before passing through a cooling ring. A comparison of film orientations in the transverse direction (TD) and machine direction (MD) shows the properties to be similar if the stretching occurs simultaneously in each direction. In sequential stretching, the last stretching step predominates, so TD is usually stronger,

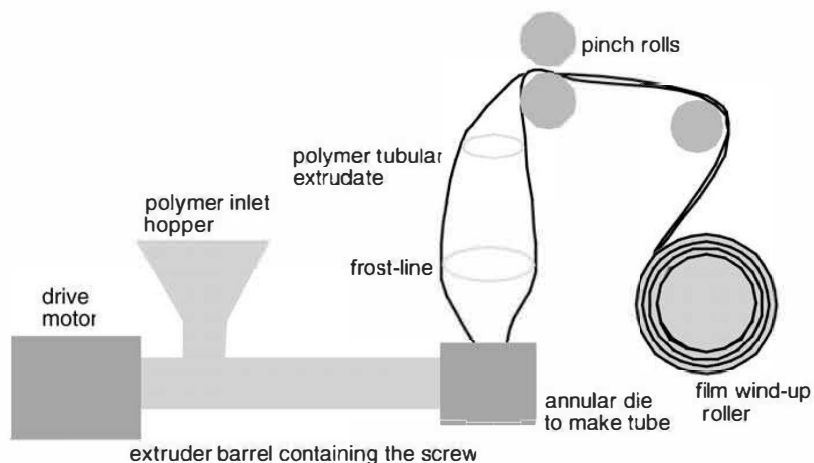


Figure 1.4 Diagram showing the extrusion blown film process

except for tear strength. Oriented PP (OPP) stretch ratios of 6 x 6 are common. Shrink films can be prepared from LLDPE and copolymers of ethylene and propylene, but radiation modification is necessary to partially crosslink the polymer.

1.5.1 Extruder Characteristics

The extruder must be able to process a wide variety of polyethylenes with varying molar mass, molar mass distribution, comonomer content and comonomer distribution. Less powerful extruders may only be suitable for LDPE production, since its shear-thinning characteristics assist high throughput at lower power. Additives such as antioxidants, ultraviolet stabilisers, lubricants, slip agents and tackifiers may need to be included at the extrusion stage, so a facility for separate injection or dry blending of these additives may be required. The extruder must provide the means to melt and convey the molten polymer through a die that will produce the film. Typically, a single-screw extruder will be suitable. There are many types of single-screw extruders, but, generally, they are best suited to distributive mixing. Distributive mixing is where the components only need sufficient mixing to provide a uniform melt. Twin-screw extruders provide more intensive mixing, and so are used when dispersive mixing is required. Dispersive mixing is where high shear is needed to subdivide a dispersed phase into smaller particles, where the dispersed phase may be another polymer or a filler with aggregated particles [11].

1.5.2 Screw Design

The extruder screw is usually divided into three zones: feed zone, compression zone and metering zone. The feed zone conveys the polymer pellets, filler and additives from the hopper into the main part of the extruder. In the compression zone, the polymer is melted, mixed with any other components and compressed into a continuous stream of molten polymer compound. The metering zone provides a uniform flow rate to convey the polymer to the die. Polyethylenes are semicrystalline polymers with a broad melting range, particularly if they are copolymers or have random branching, such as LDPE or LLDPE. The melting or compression zones of the screw must be broad. This is the region where the depth of flight is decreased to provide the compression. Polyethylenes have a higher molar mass than other polymers used for extrusion, so the melt viscosity is reasonably high. Polyolefins have weak intermolecular forces, so the mechanical properties are derived from a high molar mass and regularity of the chains for close packing. In addition to the force required for extrusion, the strength of the molten films is important in successful film formation. Of the polyolefins, polypropylene is the most difficult for film production because it has relatively low melt strength. Very high molar mass will improve the film formation, but make the extrusion part of the process more energy-consuming [10].

1.5.3 Frost-line and Blow Ratio

The molten film exits from the extruder through an annular die so that a tube of polymer is formed. The tube is sealed at the top as it passes between pinch rollers. The tube is expanded using air pressure. The tube will only expand significantly when the polymer is molten. The rate at which the polymer exits from the die, the air pressure and the impingement of external chilled air determine the blow ratio. The blow ratio is the ratio of the final tube diameter to the diameter of the annulus in the die. This ratio, together with the width of the slot in the die, determines the film thickness and the transverse orientation of the film. The film is also oriented in the direction parallel to the die by a differential between the speed of the polymer exiting the die and the speed of the pinch rollers pressing the tube flat and feeding it to the auxiliary equipment. The transverse orientation occurs up until the polymer solidifies and is often the dominant orientation for properties. The blow ratio able to be used is limited by the melt strength of the polymer. Linear polymers are more likely to exhibit film rupture in the melted region of the tube. Polymers with long branches have higher melt strength and so are much better for production of blown film. The rheology of the polymer is important for other aspects, since an unstable bubble may be formed [12]. The bubble should be symmetrical about the centre-line of the die to the pinch rollers. If the film is uneven in thickness or in solidification, then symmetry will be difficult to control. A thicker portion of the film will be stronger and will resist blowing and so remain thicker. A thinner portion of the

film will expand easier and will become thinner, so this part of the film will bulge outwards even more. The thinner part of the bubble may even rupture. Differential heater bands can be placed around the film near the exit from the extruder to provide fine adjustment of the film temperature as the film is expanded.

The frost-line is the point at which the polymer solidifies by crystallisation. The transparency of the polymer is decreased on crystallisation, and this is observed as a sharp transition in the film not very far above the die. The frost-line depends on the extrusion speed and the temperature, as well as on the cooling air that is directed on to the polymer tube from the outside. The cooling air is usually refrigerated, and its temperature, velocity and angle of impingement on to the film may all be varied. Rapid crystallisation will provide smaller crystals, and so the film will be clearer, apparent in a low haze, and have a smoother surface, apparent in a high gloss [13].

1.6 Cast Film Production

1.6.1 Extrusion Conditions

Cast film is extruded through a very thin horizontal slit die. The film is drawn from the extruder by calender rolls. This process does not expand the width nor decrease the thickness of the film, though the calendaring occurs immediately after extrusion. The extrusion process is the same as for other extrusions. The melted polymer must be distributed evenly along a slit die, usually using channels in the die. The die is referred to as a coat hanger or fish tail die. The calender rolls are chilled so that they provide a melt quenching, giving smaller crystals than the blown film process. The film has a very smooth surface due to the calendaring process [8]. The smooth surface can cause self-adhesion of the film, called blocking. An antiblocking agent may be added to reduce the blocking. Cast films will usually have superior gloss and low haze compared with blown films. Orientation of polypropylene flat film uses a tenter frame (chain) with clamps in the transverse direction, a quench roll, then reheating rolls followed by tenter and wind-up roll for the machine direction. The tenter frame is enclosed in an oven that is used to heat and relax the film [6]. **Figure 1.5** provides a schematic illustration of the cast film process.

Coextrusion is used to make multilayer films by extruding several polymers at the one time through a single complex die. Each individual polymer will have its own extruder feeding into a central die. An individual polymer may be included into more than one layer, yet it only need come from one extruder. Multilayer films are common despite the complexity of the equipment required for their manufacture. Each layer has a special

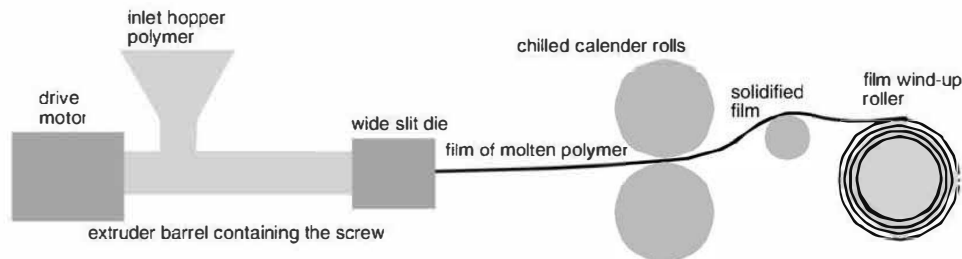


Figure 1.5 Diagram showing the extrusion cast film process with calendaring and extrusion coating

purpose in the film. The requirements for mechanical protection, diffusion barrier properties, substrate and interlayer adhesion, and heat shrinkage cannot all be met through a single polymer. The most suitable polymer for each purpose can be chosen and assembled into the multilayer structure.

1.6.2 Calendaring Finishing

The melted film is usually cooled and pressed to provide a high-quality surface by passing it through a set of chilled calender rollers immediately after extrusion. The rollers will be of highly polished steel to provide a smooth glossy surface to the film. Rapid cooling also assists formation of a glossy surface on the film, since the crystals will be kept small and crystallisation may be minimised. A series of rollers may be used to provide orientation by stretching the film in a longitudinal direction.

1.6.3 Extrusion Coating

Extrusion coating is when the melted polymer film is extruded on to an existing film before passing through the calender rollers. The existing film will be another polymer, metallic foil or paper. Multiple layers may be formed by extrusion coating both sides of the primary film or building a multilayer structure by introducing several extrusion-coated layers. Coextrusion can only be used for polymers with similar processing conditions. Where the processing conditions are different, particularly in the case of substrates that cannot be melted with the polymer, such as metallic foils and paper, then extrusion coating is the only choice [6].

1.7 Orientation of the Film

1.7.1 Orientation During Blowing

Extrusion blow moulded film usually receives biaxial orientation. During blowing, the diameter of the extruded tube is increased, and this causes the structure of the film to be oriented perpendicular to the extrusion direction. Orientation should take place below the melting temperature when the polymer is crystalline so that the crystals are oriented. The expansion of the extruded tube will take place while the polymer is entirely melted, so that the effect of blowing will not provide a level of orientation equivalent to the diameter expansion [14].

At the same time as the film is being expanded by blowing, it is being drawn by pulling along the axis of extrusion. This provides a parallel orientation. Again, most of the parallel drawing occurs on the polymer melt between when it leaves the extruder and when it crystallises. The crystallisation region is called the frost-line. At the frost-line the film will have its maximum diameter and resist further expansion or drawing compared with the region immediately before the frost-line. At the frost-line the completely transparent melt becomes foggy due to crystallisation. The change in opacity depends on the crystallinity of the particular polymer.

Sometimes additional orientation is imparted on the film after the blowing process. This is the case if the film is to be a shrinkable film. Shrinkable films will contract upon heating. This is useful for providing tightly fitting wrapping.

1.7.2 Orientation by Drawing

Orientation of a polymer must be performed at a temperature between the glass transition and melting temperatures. Polyolefins, particularly polypropylene, are normally moderately heated. The enhancement of tensile properties is directly related to the draw ratio. After drawing, the film should be further heated to relax or set the structure. This will provide dimensional stability. If the film is to be heat-shrinkable, then the relaxation is not performed. Some crosslinking from radiation treatment prior to drawing may be used to increase the plastic memory effect in the film. Excessive drawing can cause strain hardening because of the introduction of extended chain crystals at the expense of chain-folded crystals. The strain-hardened film will have a stiffer or more leathery feel; it will lose elasticity and may have a rougher surface.

1.7.3 Biaxial Orientation (Biaxially Oriented PP, BOPP)

It is desirable to orient films in planar directions, parallel and perpendicular to the flow. The parallel orientation can be provided by a draw-off faster than the extrusion speed.

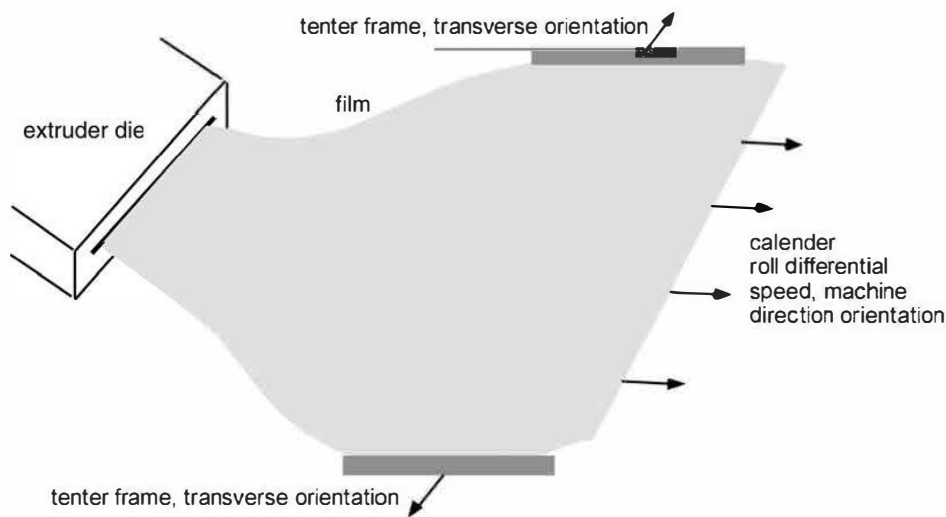


Figure 1.6 Schematic diagram for biaxial orientation of cast film

The perpendicular direction has been described for blown film production. In extruded sheet, a frame that attaches to the edges of the film and moves apart must provide the perpendicular orientation. This is called a tenter frame. The film is often drawn to about three times its original width. As well as adding strength to the film, a thinner gauge of film can be produced. The drawing process overcomes the effect of die swell that occurs as the film leaves the die. Orientation of cast film is illustrated in **Figure 1.6**.

1.8 Surface Properties

1.8.1 Gloss

Gloss is the reflection of light from a surface. The nature and origin of gloss and haze are illustrated in **Figure 1.7**. A high gloss requires a smooth surface. Surface imperfections may be introduced by the processing. Excessive drawing into the strain-hardening region will usually reduce the gloss. Blown film usually has a lower gloss, since crystallisation of the film at the frost-line introduces surface roughness due to the crystals. Rapid crystallisation of the film by the use of chilled air impinging on the bubble reduces the size of crystals and improves the gloss. Extrusion cast film passes through chilled rollers after leaving the

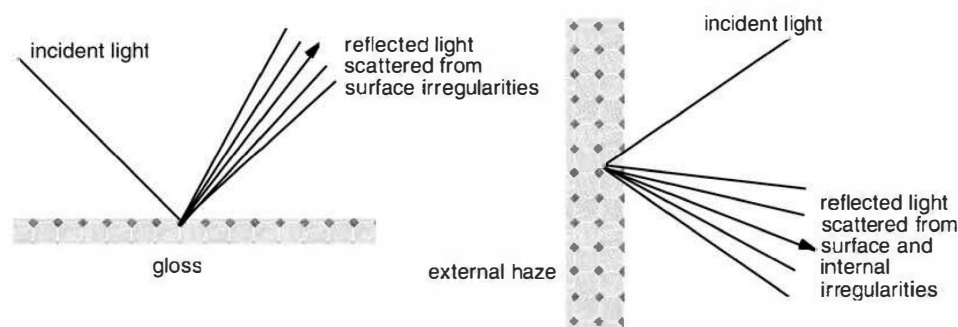


Figure 1.7 Diagram showing the origin of gloss and haze in polymer films

extruder. The rapid cooling and the polished surface of the rollers provide a high-gloss surface. Extrusion cast films have the higher gloss, but the extrusion blown process produces film at a lower cost. The rheology of the polymer will contribute to the surface of the film. Shark skin is the term applied to a rheological problem in the processing [15].

1.8.2 Haze

Haze is an internal bulk property, but, because of the importance of appearance, it has been considered along with surface properties due to its relation to gloss (see **Figure 1.7**). Crystallinity, optical defects, 'fish eyes', phase separation of blends, contaminants, gel particles and dispersion of pigments (carbon black) are structures that increase haze. Haze is the internal scattering of light. Haze makes it difficult to clearly see an object through a film as a result of the interference from randomly scattered light reaching the viewer in addition to light coming straight from the object. Smaller crystals provided by a nucleating agent will decrease haze. The other phenomena described above can also be reduced by nucleating agents, better formulation and processing.

1.8.3 Surface Energy

The surface energy of polyolefin films is very low. It is difficult to find other substances that will adhere to polyolefins. Suitable adhesion can be obtained by melt adhesion of polyolefins to each other, but only when the polyolefins are very similar. For instance, polyethylenes have good mutual adhesion. The branched polyethylenes with lower melting temperature are most used because they can be melted more rapidly and they have suitable

rheology to flow on to the adherend. Melt adhesion of films will require higher-melting layers other than the surface layer, since if more than the surface layer melts then the structural integrity of the film will be destroyed.

Copolymers of ethylene with vinyl acetate, methyl acrylate, acrylic acid, maleic acid and many other polar monomers are used to increase the surface energy of polyethylenes to make them more readily wettable. Similarly, polypropylene can be grafted with maleic anhydride to increase the adhesion of other substances to it. The surface energy of polyolefins is also increased through corona discharge treatment.

1.8.4 Slip

Polyolefin films generally have a smooth surface, with the exception of defects and surface crystal structures. They have a low surface energy and so frictional forces are low. Relative to their strength, the frictional forces can cause damage to the films. Slip additives can decrease the frictional forces. The factors that cause poor slip are often desired for other attributes such as adhesion of printing and adhesion to other surfaces in packaging. Additives that increase self-adhesion of packaging films will decrease the slip, so that desirable properties are not universal – they depend on the intended application of the film.

1.8.5 Blocking

The low surface energy and softness of polyethylenes make them self-adhere if pressed together under a load for a considerable time. This self-adhesion is called blocking. The polyolefins can flow, or creep, under load, and so mutual adhesion can occur if the pressure is sufficient or the time of contact is long. This is a significant problem in large film rolls or when film is stacked in large quantity. Blocking is reduced when the surface is less smooth, such as when crystallisation or processing conditions cause microtopographies. A smooth surface with high gloss and clarity is generally preferred, so that blocking will be a serious problem.

1.9 Surface Modification

1.9.1 Corona Discharge

Processes for modifying the surface properties of plastic films are important. Surface adhesion can be increased by oxidative treatments such as corona, flame, priming or subcoating. Corona discharge is most widely used, and surface oxidation of the film

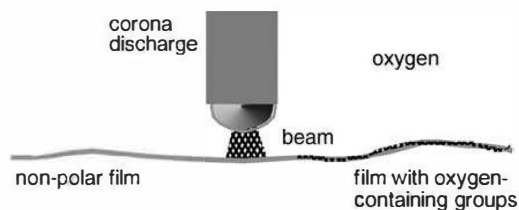


Figure 1.8 Corona discharge surface treatment system

occurs, giving polar functional groups [16]. A corona discharge treatment facility is shown in **Figure 1.8**. Increased polarity will increase the surface energy and enable wetting by inks or adhesives. Printing is carried out by the flexographic technique, whereby a rubber roller with raised imprints imparts the ink, or by the rotogravure process, whereby an engraved steel roller imparts the ink. Film coating, film wetting, dispersion coating (by an emulsion), solvent coating, barrier and heat seal coatings are all improved after oxidative surface treatment. Extrusion coating is the process whereby a film is extruded on to an existing film. Film lamination occurs when existing films are bonded together with an adhesion layer applied by any of the previously mentioned methods. Typical are the use of poly(vinylidene dichloride), aluminium foil and ionomer films, and metallisation by vapour deposition of aluminium. Coextrusion is the process in which two or more films are extruded and brought together in the die. Each layer will contribute to specific properties, such as barrier and adhesive layers.

1.9.2 Antiblocking

Blocking can be reduced by decreasing the surface contact area of the films. Small particles at the surface can decrease the contact. Particles such as silica, diatomaceous earth and talc are useful antiblocking agents [17]. To provide the protection efficiently, they must be included in the polymer during processing. Many of the particles will be in the bulk of the film, so they will not contribute to antiblocking characteristics. Those particles that exist at the surface will be active. The particles must be small enough not to introduce haze when in the interior or decrease gloss when at the surface. Films that have a rougher surface due to surface crystallites or other imperfections will have a natural protection against blocking. The mechanism of antiblock additives is shown in **Figure 1.9**.

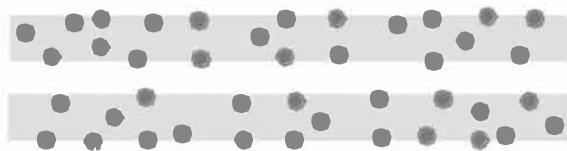


Figure 1.9 Mineral particles (silica or talc) prevent blocking, since some particles become located at the surface and so limit contact of the films

1.9.3 Slip Additives

The coefficient of friction can be reduced by adding slip agents. The requirement for a slip agent is that it is miscible with the polymer melt, but separates as the polymer is crystallising. Sometimes the separation will take several hours or days to become complete. The slip agent should form a very thin layer on the surface. The layer is more effective if it is randomly structured. The mutual miscibility and separation are important, and long-chain amides have been found to be best when the chain length is about 22 carbon atoms, whereas 18 carbons is less effective. An amide with a *cis* double bond is better than the fully saturated analogue because the *cis* double bond prevents surface crystallisation of the amide compared with the saturated amide. Erucamide has thus been found to be the most effective slip agent for polyolefins [18]. Other fatty amides such as ethylene bis-stearamide, oleamide and stearamide have been used. The function of a typical slip additive is shown in **Figure 1.10**.

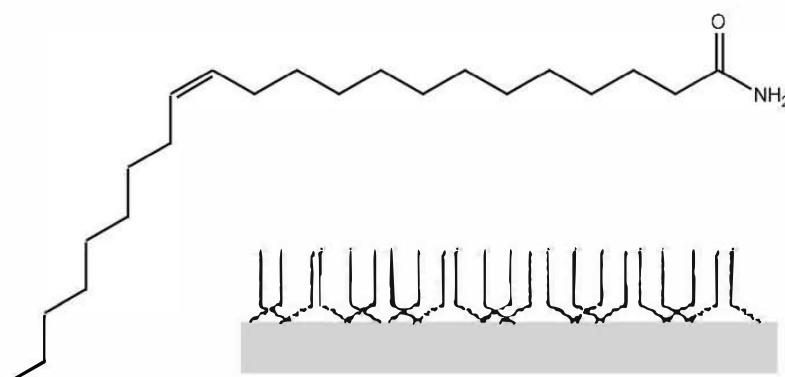


Figure 1.10 Structure of erucamide ($C_{21}H_{41}CONH_2$, *cis*-13-docosenamide) slip additive, and its mechanism for increasing slip. The diagram shows an array of erucamide molecules along the surface of a film, with the bent *cis* structure ensuring that they stay irregular

1.9.4 Lubricants

Lubricants are added to assist with processing. The polymer can be extruded more readily when there is a layer of lubricant between the polymer and the surfaces within the extruder. This is particularly important at the die lips, where the lubricant can decrease surface irregularities such as 'shark skin' effects. The melt can maintain laminar flow at higher extrusion rates with lubricants present. Common lubricants are stearic acid, stearate salts, paraffin wax and chlorinated paraffins [19]. A fluoropolymer has been reported as a processing additive for polypropylene [20].

1.9.5 Antistatic Agents

Polyolefins do not absorb water. The dry surface causes a build-up of static electricity. Antistatic agents are polar substances that are mixed with the polymer and migrate to the surface after the polymer emerges from the extruder. Polyoxyethylenes are one type of antistatic agent. When on the surface, they can absorb sufficient water to prevent static electricity build-up. A problem is that they can attract dust and other materials that would not normally adhere to the polyolefins. Another problem is that they can be easily removed by friction or extraction with polar liquids [19].

1.10 Internal Additives

1.10.1 Antioxidants

Immediately the polyolefin is made, it requires protection from oxidation. This is particularly the case during the processing stages when high temperatures are used. Hindered phenols and triaryl phosphites are typically used. During the extrusion process, the polyolefin is then protected from the heat and oxygen. During the lifetime of the film, other thermal processes may be encountered during printing, packaging of food and heat sealing. The antioxidants act by removal of radicals from the polymer – by hydrogen donation in the case of hindered phenols, and by removal of oxygen from peroxy groups in the case of phosphites [18]. **Figure 1.11** shows a typical hindered phenol antioxidant and a triphenyl phosphite secondary antioxidant.

1.10.2 Ultraviolet Absorbers

Films that are to be used in the sunlight require protection. While the polyolefins do not absorb ultraviolet light, they do contain many other anomalous functional groups, additives and impurities that do absorb. Hydroxybenzophenones, hydroxybenzotriazoles

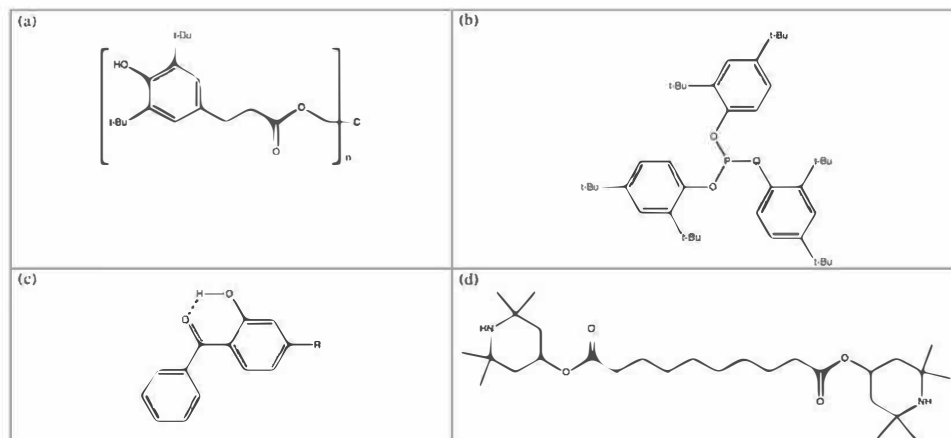


Figure 1.11 Structures of common heat and light stabilisers: (a) hindered phenol antioxidant; (b) tris(2,4-di-*tert*-butylphenyl) phosphite secondary antioxidant; (c) hydroxybenzophenone ultraviolet absorber; (d) hindered amine light stabiliser

and tetramethylpiperidines (hindered amine light stabilisers, HALS) are typical compounds used for ultraviolet stabilisation. Factors such as compatibility with the polyolefin, low volatility and absence of any colour are just some of the many stringent requirements of these additives. Hydroxybenzophenones and hydroxybenzotriazoles absorb ultraviolet light and form an excited electron state that can undergo a radiationless transfer of the energy to heat, to regenerate the ground state. HALS act by a cyclic mechanism in which they form a nitroxide that can couple with a radical and then transfer the radical to terminate another radical and release the nitroxide. HALS are the most effective stabilisers for polypropylene, but the type of HALS used depends on the application of the polypropylene and the other components in the composition [17]. **Figure 1.11** shows a typical hindered amine light stabiliser and a hydroxybenzophenone ultraviolet absorber.

1.11 Mechanical Properties

There are many standard test methods to define the performance requirements of polyolefin films. These are specified in the relevant ASTM, DIN and ISO standards. The material mechanical properties are used for polymer specification for a particular purpose. There are many tests available, and each measures a narrowly defined property. Often it is difficult to predict performance by a material property, and so a product-specific test is designed.

The mechanical properties can be separated into tensile and impact tests, though there are many other tests, such as tear testing, abrasion resistance and adhesion tests. The morphology of the film is of major importance in controlling the mechanical properties [21]. The morphology of a film is strongly connected with the key processing variables [8].

1.11.1 Tensile Properties

1.11.1.1 Strain Rate and Tensile Properties

The strain rate is important in measuring the tensile properties of films. During packaging operations, films are often subjected to extremely high strain rates in the machinery. These processes must be duplicated in the testing procedures where possible. Slow strain rates may be preferred when material properties are measured to distinguish between various polyolefin structures. Typical parameters that are obtained from a tensile test are the modulus, yield stress, break stress and elongation at break. The area under the stress-strain curve is used as a measure of the energy to break.

1.11.1.2 Strain Hardening

When a polyolefin film is considerably extended, the crystal structure orientation will be significant and the polymer will become harder. Often a strain-hardened film is described as leathery. The morphology may change from a chain-folded to an extended-chain configuration. The tie molecules become fully extended so that further strain is limited before film breakage occurs. Strain hardening is a limit to the useful elongational performance of a film because the elasticity is lost. A stress-strain curve for linear low-density polyethylene showing the yield and strain-hardening regions is shown in **Figure 1.12**.

1.11.1.3 Stress Relaxation

Stress relaxation is defined as a change in stress when the material is under constant strain. When a packaging film is stretched around an article, or a large number of articles, the elasticity of the film will keep the article(s) under constant tension to provide protection and ease of transport and handling. When stress relaxation occurs, the tension of the packaging is lost, and the contents are no longer held together. Stress relaxation can be measured with a standard tensile testing instrument, where the stress is measured over time while the specimen is held under a constant strain. Polyolefins with high molar mass and high crystallinity will be the most resistant to stress relaxation. An illustration of the processes involved in stress relaxation is shown in **Figure 1.13**; first the amorphous molecules are elongated, then on relaxation they slide past each other to return to a random-coil conformation.

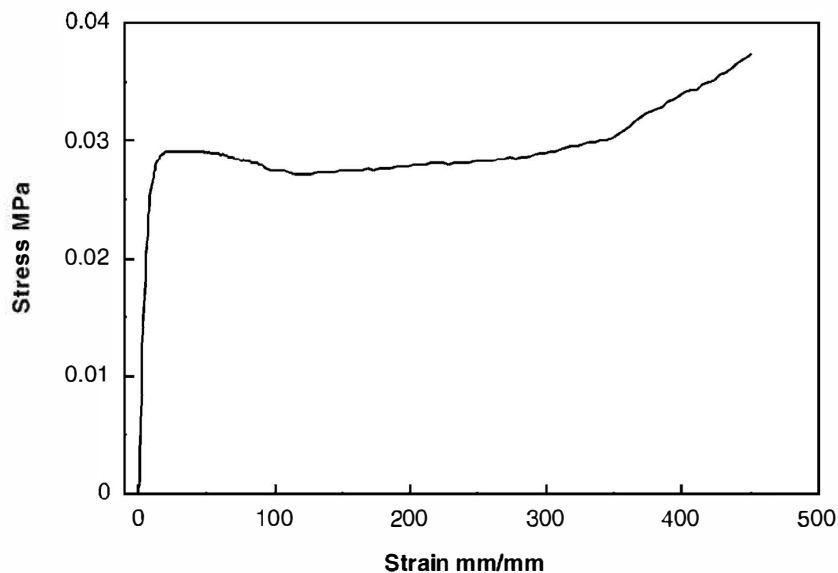


Figure 1.12 Stress-strain curve for linear low-density polyethylene showing the yield stress after the initial linear elastic region, then the strain-hardening region after 350% strain

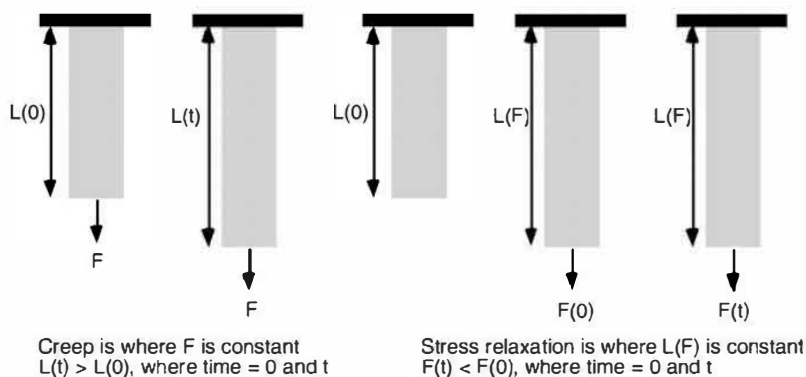


Figure 1.13 Schematic for the mechanism of creep and stress relaxation

1.11.1.4 Creep

Creep is the change in strain when the specimen is subjected to a constant stress. Polyolefin films that are exposed to pressure for extended periods will gradually elongate. Pressures

are generated inside many packages, and polymer will creep, causing the package to become larger. Creep is a complementary property to stress relaxation, and so the same molecular characteristics resist creep. Creep is illustrated in **Figure 1.13**; under constant load the molecules gradually slide past each other, resulting in elongation.

1.11.1.5 Burst Strength

When a film experiences a high pressure over a short time, it may burst. This is similar to elongation at break, except that the film will be under a biaxial tension. A test of burst strength may be more suitable for a film under pressure than a tensile test. The short-term nature of the test is in contrast to the long time for creep.

1.11.2 Impact Properties

1.11.2.1 Dart – Puncture Resistance

An impact test is a short-term test; the stress is applied very quickly. The dart test can involve either a dart falling through a constant distance or a dart propelled by gas pressure. The shape of the end of the dart is an important factor in the test. A rounded end is generally used, but the test can be modified to measure the resistance of a film to any puncture by impact with any particular object. The falling dart test will result in a pass/fail type result compared with a specification for the load. The instrument can be designed to measure the deceleration of the dart as it passes through the film. The energy required to break the film is then calculated from the energy lost by the dart. In this latter situation, the dart is always required to break the film.

1.11.2.2 Tensile – Tear Strength

Films often break in shear instead of tension. A film can be tested in a tensile instrument so that the strain is applied under shearing conditions. A cut may be made in the film to direct the tear. The geometry and conditions of the test are defined so that standard conditions are used. The Elmendorf tear strength test is used to measure the performance of films, and it has been related to processing conditions and dart impact strength [22].

1.11.2.3 Tensile Impact

This is a short-term impact test where the specimen is mounted in a pendulum test instrument so that it receives a rapid tensile force as the pendulum strikes the specimen

holder. The tensile impact test is applicable to films, whereas other forms of pendulum impact tests, such as Izod and Charpy tests, require more rigid specimens. The tensile impact test can apply a greater strain rate than a typical tensile test instrument.

1.11.3 Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) measures the properties when an oscillating stress is applied to the material. The stress and strain are often out of phase, and this situation can be used to obtain the viscoelastic properties. The viscous or time-dependent properties are out of phase with the stress, while the elastic or instantaneous properties are in phase with the stress. The in-phase property is called the storage modulus, in that the elastic energy is stored and can be subsequently released when the stress is removed. The out-of-phase property is called the loss modulus, in that energy is lost to heat during viscous flow. The properties are usually measured with temperature and/or frequency. Temperature and frequency can be combined to provide a time-temperature transposition, so that long-term or very short-term properties can be measured within real-time limitations [23]. Figure 1.14 shows DMA curves for polypropylene.

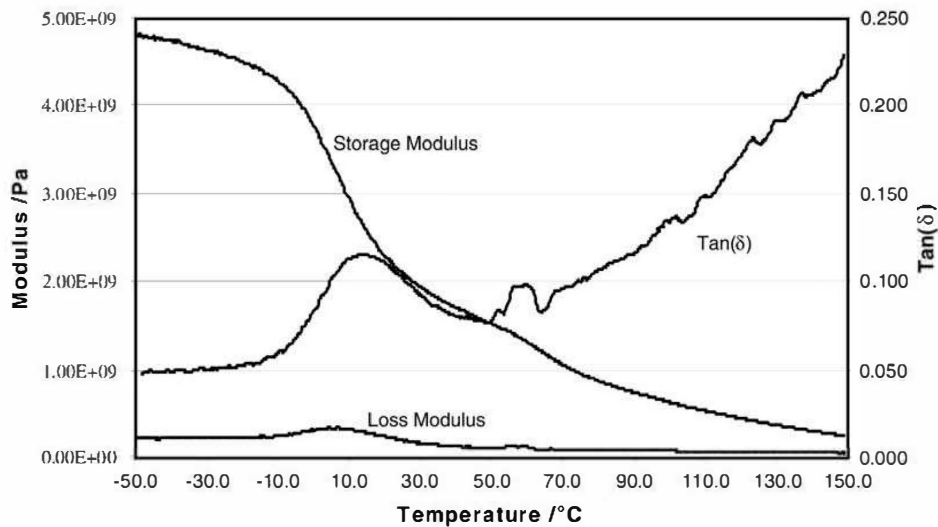


Figure 1.14 DMA curve for polypropylene, showing the storage modulus, E' , loss modulus, E'' , and damping factor, $\tan \delta$

1.11.4 Dielectric Properties

Polar olefin copolymer films, such as poly(ethylene-co-vinyl acetate), poly(ethylene-co-methyl acrylate) and poly(ethylene-co-butyl acrylate), and blends or laminates can be characterised using dielectric analysis. The dielectric properties of all types of polyolefins are important because of the electrical applications of these polymers. However, dielectric analysis can also be performed in an analogous manner to DMA, in that the mechanical force is replaced by a voltage and the permittivity is measured while the temperature and/or frequency is varied. The viscoelastic properties of the polymer can be measured by the dielectric response over a wider range of frequencies than the mechanical tests. The dielectric test is more sensitive than the mechanical test when the polymer has more polar groups. **Figure 1.15** provides a schematic of the processes involved in a typical dielectric analysis.

Capacitance (C) I = current V = voltage f = frequency δ = phase angle	$C = \frac{I \sin \delta}{V 2\pi f}$
Conductance (R^{-1})	$R^{-1} = \frac{I \cos \delta}{V}$
Permittivity (ϵ') ϵ_0 = permittivity of a vacuum, A = area of electrode D = distance between electrodes	$\epsilon' = \left(\frac{C}{\epsilon_0} \right) \left(\frac{1}{A/D} \right)$
Loss factor (ϵ'') ω = angular frequency σ = conductivity	$\epsilon'' = \epsilon''_{dipole} + \frac{\sigma}{\omega \epsilon_0}$

Figure 1.15 Dielectric analysis of polar ethylene copolymers involves measurement of the storage (permittivity) and loss (loss factor) components with temperature

1.12 Microscopic Examination

1.12.1 Optical – Polarised Light Effect with Strain

The crystallinity of a polyolefin in a film can be viewed with an optical microscope using polarised light. The film must be very thin, although reflected light can be used for thicker opaque films. The microscope can be combined with a hot stage to view crystallisation and melting events.

1.12.2 Scanning Electron Microscopy (SEM) – Etching

Scanning electron microscopy (SEM) can reveal morphology, though usually the sample must be etched so that amorphous regions are modified more than crystalline, or a component in a blend is eroded more rapidly. The etching creates a new surface topography that can be viewed with the SEM. Care must be taken so that the electron beam does not damage or create artefacts on the surface.

1.12.3 Atomic Force Microscopy (AFM)

The surface of polyolefin films can reveal information about the bulk. Crystal growth at the surface and other irregularities that may arise from processing or treatments such as corona discharge can be studied using atomic force microscopy. Variations in the hardness or friction across the surface as found in blends can be studied to reveal the distribution of components across the surface. **Figure 1.16** shows an atomic force microscope picture of the surface of linear low-density polyethylene formed by the extrusion blow moulding process.

1.13 Thermal Analysis

1.13.1 Differential Scanning Calorimetry (DSC)

DSC is used to measure the crystallisation and melting temperatures of polyolefins as well as the enthalpies of crystallisation and melting. The results shown in **Figure 1.17** are used to identify, characterise and measure the crystallinity [24]. The thermal history and mechanical stresses of a film can be investigated through the melting and crystallisation response measured by DSC [25]. The crystallisation temperature increases with nucleation, so that the efficiency of added nucleation agents can be measured. The crystal structure varies with processing conditions and other treatments such as orientation, and these can be measured by analysis of the melting of the polyolefin on heating.

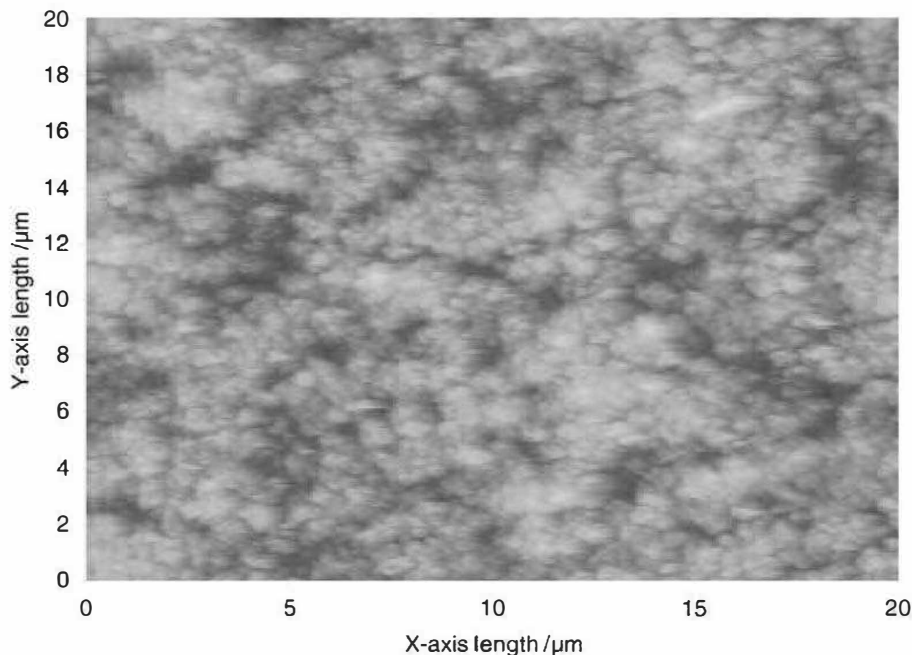


Figure 1.16 Atomic force microscope picture of the surface of linear low-density polyethylene film prepared by the extrusion blown film process

1.13.2 Temperature-Modulated DSC (TMDSC)

TMDSC is analogous to DMA in that an oscillating force, in this case a temperature programme, is applied to the sample. The response can be resolved into reversing and non-reversing specific heat capacities. Recrystallisation, rearrangement of the crystals and melting can be studied simultaneously. This is important for an understanding of the equilibration of the morphology of the polyolefins after various processing or other thermal treatments [26].

1.14 Infrared Spectroscopy

1.14.1 Characterisation

Infrared spectroscopy is a convenient method to identify polyolefin films. The main classes of polyolefins can be easily identified. A detailed interpretation of the infrared spectrum

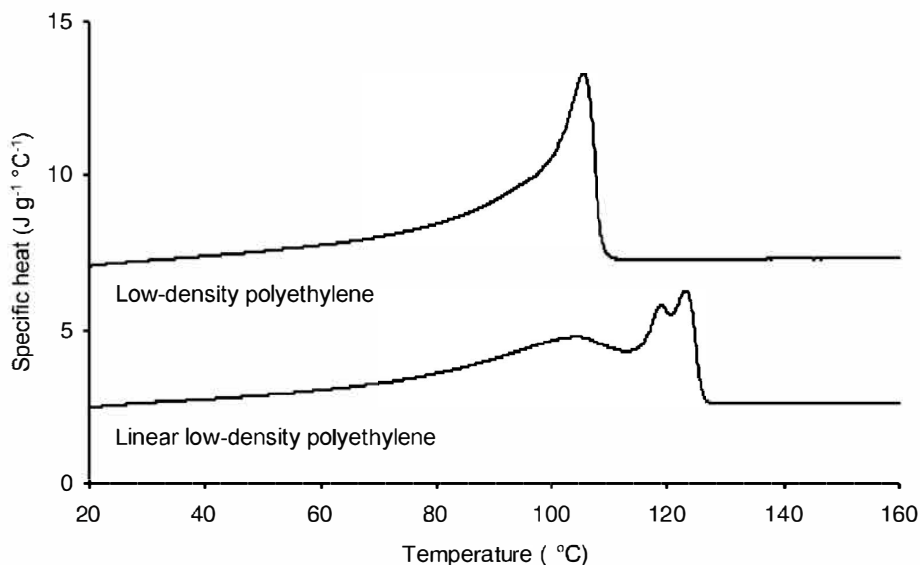


Figure 1.17 DSC curves for melting of linear low-density polyethylene and low-density polyethylene (for clarity, this curve has been shifted upwards by five units)

will enable even very similar structures to be distinguished. The extent of branching can be measured and crystallinity can be indirectly measured [27].

1.14.2 Composition Analysis of Blends and Laminates

Blends of polyolefins can be identified, and, when the components are known, quantitative analysis can be performed. The component layers of laminates can be identified after separation of the layers, or by analysis of the edge of the film using an infrared microscope.

1.14.3 Surface Analysis

Surface additives, such as glyceryl monooleate, polyisobutylene and slip agents, and corona treatments can be measured using surface infrared spectroscopic analysis. Multiple internal reflection is the common method, but specular reflectance and grazing angle reflectance are other useful techniques by which the infrared spectrometer can be used to study surface chemistry. Figure 1.18 shows a schematic for the surface analysis of a polymer

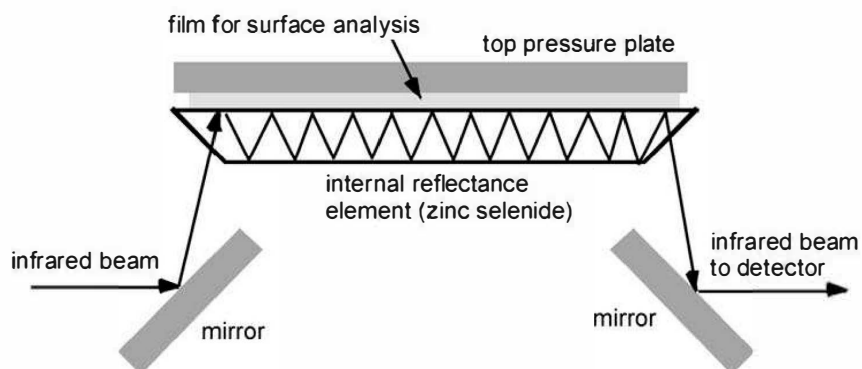


Figure 1.18 Apparatus for multiple internal reflectance (attenuated total reflectance) infrared spectroscopy for surface analysis of polymer films

film by multiple internal reflection. The angle of the infrared beam to the surface of the internal reflectance element (typically zinc selenide or germanium) along with the wavelength of the infrared beam determine the depth of penetration into the surface of the film. A low depth of penetration will provide spectra more sensitive to the surface additives or modifications.

1.14.4 Other Properties

1.14.4.1 Thickness

Thickness is known as gauge. Uniformity must be achieved by the manufacturing process. Generally films are considered to be of $\leq 250 \mu\text{m}$; greater thicknesses are called sheet. Some films may be 10-20 μm in thickness, and individual layers in multilayer films are often only 5 μm thick.

1.14.4.2 Moisture Resistance

Polyolefins are nonpolar, so they are particularly efficient at resisting moisture. Their resistance to liquid water is not necessarily carried on to their resistance to water vapour or humidity. High-density polyethylene film is the most resistant to water vapour because gas molecules have difficulty diffusing through the crystalline structure.

1.14.4.3 Gas Permeation

Films are used to encase and protect other items. An important property is to resist gas permeation, in particular, the permeation of oxygen, carbon dioxide and water vapour. Polyolefins provide very poor barrier layers. Usually a multilayer film that includes another polymer or other material is required to provide suitable barrier properties. The barrier properties are increased when higher-crystallinity polymers are used. The density of the amorphous phase of the polymer has been found to be a guide as to the permeation resistance [28].

1.14.4.4 Orientation

Orientation of a film may be measured by annealing the film at temperatures below the melting temperature. Oriented films will shrink more than others. The shrinkage is often controlled by partial crosslinking of the film. There are many applications in the food industry for shrink-wrapping of produce. Shrink-wrapping of polyethylene films can be applied over other packaging materials to group containers into specific quantities.

1.14.4.5 Dimensional Stability

Dimensional stability is usually a consequence of orientation. Under heat treatments such as may be experienced during packaging of hot foods, sterilisation processes for foods and heat sealing, the dimensional stability of the film must be maintained. This is the opposite requirement to shrink-wrap films. Humidity can contribute to changes in dimension, due to absorption of moisture by other components of a multilayer film or by the contents of the film package.

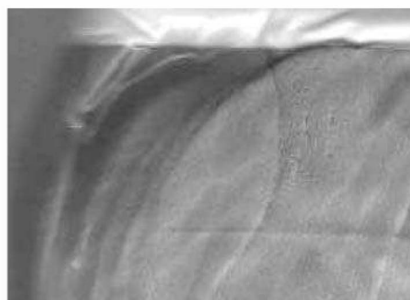
1.15 Applications

1.15.1 Packaging

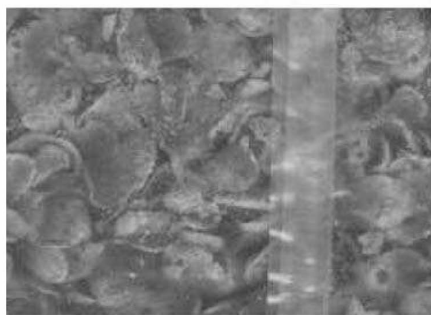
The main application of films is for packaging (**Figure 1.19**). The functions of a package can be summarised as: containment, dispensing, preservation, protection, communication and display. Packaging machinery is diverse, (e.g., vertical fill, shrink-wrap, sleeve-wrap, stretch-wrap and blister packaging machines), and thus requires many properties of the film, (e.g., stiffness, stretchability, heat sealability), which in addition must be suitable for various applications, (e.g., in side weld bags, in bottom seal bags and to hold liquid



A sterile eye pad in a heat sealed film



Bacon in a vacuum sealed transparent film



Corn flakes in high-density polyethylene



Rice in a clear polyethylene printed film

Figure 1.19 Examples of typical packaging applications for polyolefin films

products). Many of the films are required to be multilayer films to achieve all of the desired properties [14]. Polyethylenes with new improved properties due to high molar mass are being used in heavy-duty applications [29].

1.15.2 Laminated Films

The performance requirements for packaging are increasing, with new demands for protection of the product, speed and ease of packaging and sealing, together with printing, handling and storage requirements. An individual polymer cannot meet all these requirements, so multilayer films are necessary. These can be prepared by extrusion of further layers on to existing films or adhering existing films together. This process is called lamination. Most of the layers are polymer, but a metal foil (usually aluminium) may be used. Paper or paperboard is frequently used as substrates for the lamination. A textile layer may be used, but these are mainly classified separately from laminated films.

A basic requirement for a laminated film is good adhesion between the layers. The materials in the layer will often be chemically different, to provide the diversity of properties, and so adhesion may not be suitable. In such cases, a separate adhesive layer must be included between the functional layers. The adhesive layer functions in the same way as a compatibiliser in polymer blends. Often a copolymer will be used, where each of the component monomers will contribute to the adhesion with one of the adjacent layers. Some multilayer films are produced with the adhesion component included as a blend with a functional layer. In this way the number of individual layers is reduced, simplifying the lamination process.

The separate layers of the film may consist of the same polymer but in different forms. A layer could be mineral-filled, pigmented, foamed, oriented, radiation or chemically crosslinked, include antioxidant or ultraviolet stabilisers, be printed or otherwise modified. A further protective layer may then be placed over the modified layer, or the modified layer may be the protective layer.

Lamination of films is often preferred to application of a polymer layer as a lacquer since the latter includes solvent or an emulsion is used, so that drying and removal of volatiles is required. The laminated film will often have superior gloss such as when polypropylene is laminated on to printed paper substrates. Surface spreading by the coating layer and film thickness will be easier to control by laminating than by solution coating. Ovens and solvent removal systems can be replaced by calender cooling rollers.

1.15.3 Coextruded Films

Coextruded films contain most of the characteristics of laminated films, except that all of the layers are formed by extrusion at the same time. This precludes aluminium foil, paper and textile layers, which must be included by lamination. The coextrusion requires several extruders with a common die. The die has a complex construction and may be of either a tubular film type or a cast film linear slit type. The polymer for each layer is fed into the die by a separate extruder. One extruder per layer may be used or, if more than one layer contains the same polymer, then its extruder can feed into more than one layer. The latter connection uses the minimum number of extruders, but is less flexible than the 'one extruder per layer' configuration.

After coextrusion, all of the layers must receive any treatments together. For instance, if a layer is to be biaxially oriented, then all layers must be oriented. If a layer is to be radiation-crosslinked, then all of the layers must receive the radiation treatment. Individual layers cannot be printed, then covered with another protective layer. An advantage is that the complete multilayer film is produced in one process. The process is not suitable for polymers with significantly different processing temperatures. Shrinkage stresses may occur on cooling and so layers may separate.

1.15.4 Heat Sealing

Polyolefin films are joined by heat sealing, a process whereby the film is partially melted while pressing against the other component for a well-defined short time. The strength of adhesion is characterised by the time-temperature-pressure relationship and the proportion of the polymer melted. Melting will destroy the original crystal structure and any orientation in the film, so the mechanical properties will be changed. A multilayer film is preferred so that only the surface adhesive layer is partially melted, while the structural layer is unaffected. This requires that the surface layer have a lower melting temperature than the structural layer [30].

Typically, if the structural layer is polypropylene, then the surface layer can be an ethylene-propylene random copolymer, with a small proportion of ethylene. The adhesive layer may also be grafted with maleic anhydride to provide better adhesion to polar substrates. If the structural layer is a polyethylene, such as LLDPE, then the adhesive layer can be an ethylene copolymer, such as poly(ethylene-co-vinyl acetate). Recently VLDPE have been used as adhesive layers where low surface energy for better wetting is important.

1.15.5 Agriculture

Films for agriculture have become important to protect crops and to protect and bind products. The very thin films can provide sufficient tensile strength to contain the product, and with self-adhesion of the film the wrapping process is very efficient. The films may be pigmented black to protect the contents from sunlight. Pigmented film may be spread on the ground to control weeds by removal of sunlight and reduce evaporation of water [31].

1.16 Conclusion

Polyolefin films are complex in their manufacture by the blown film extrusion and extrusion cast film processes. The films are typically strengthened by biaxial orientation and can be made very thin. The inert polyolefin surface is often modified by oxidation to provide polar groups for adhesion, and by the use of additives to provide slip or to prevent blocking. Specialised properties such as gas barrier, printability, heat sealing and shrinkability are achieved by coextrusion or lamination of films with different chemical structures. The diversity of films available may seem simple, but when the details are considered even a common packaging film involves a complex range of technologies. Further advances will enable films to possess even more specialised functionality while being thinner and stronger.

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