

Handbook of Plastic Films

Editor:
Elsayed M. Abdel-Bary

Rapra Technology Limited

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Preface

The plastic industry continues to grow very rapidly and plays an important role in many fields such as engineering, medical, agriculture and domestic. It is now very difficult to find the point at which plastic cannot be considered as an essential component. The understanding of the nature of plastic films, their production techniques, applications and their characterisation is essential for producing new types of plastic films. This handbook has been written to discuss the production and main uses of plastic films.

Chapter 1 deals with the various types of polyolefins and their suitability for film manufacture. 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 particularly important applications that require special structures or modifications are given.

In Chapter 2, the main parameters influencing resin basic properties are described. The methods of processing of polyethylene films such as cast film extrusion, blow extrusion of tubular films are discussed. Effects of extrusion variables on film characteristics and effect of blow ratio on film properties are considered.

Chapter 3 details the structure, synthesis and film processing of polypropylene. The effects of some additives and UV stabilisers are discussed.

The solubility of additives plays an important role in determining the efficiency and the properties of the films as well. For this reason Chapter 4 deals with different aspects of additives solubility in polymers in relation to the polymer degradation and stabilisation.

The topic covered in Chapter 5 is the stability of polyvinyl chloride (PVC) films during processing and service. The possibility of increasing the intrinsic stability of PVC during processing with the minimal contents or in total absence of stabilisers and other additives is discussed.

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.

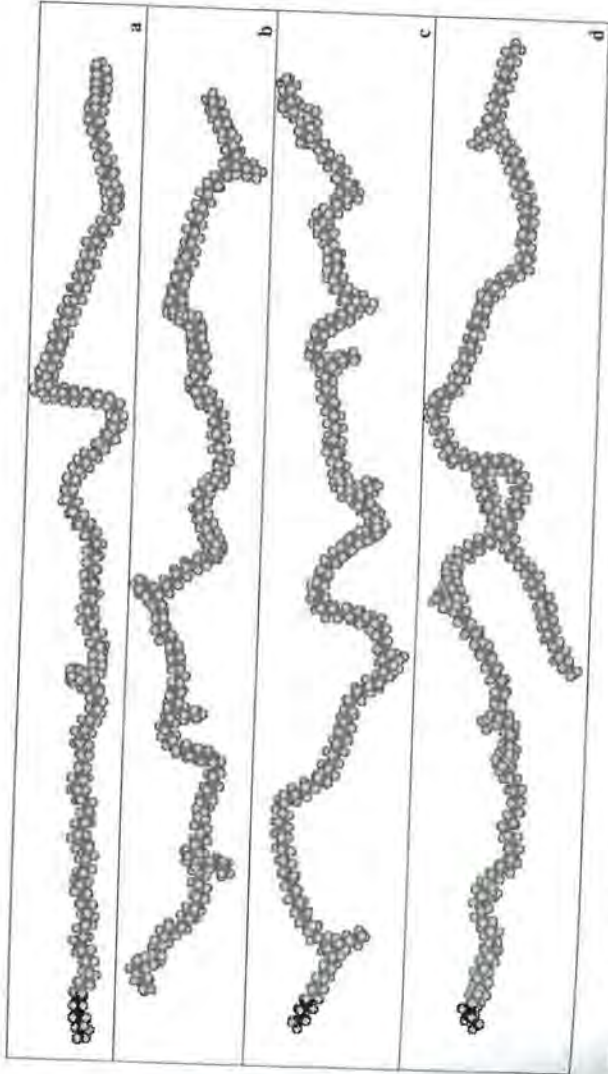


Figure 1.1 Molecular structures for linear and branched polyethylenes (LPE and BPE) with 100 monomers, four or eight short branches, and one long branch of 40 carbons: (a) LPE (100); (b) BPE (4, 100); (c) BPE (8, 100); and (d) BPE (8, L1(40), 100)

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 branches 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

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,

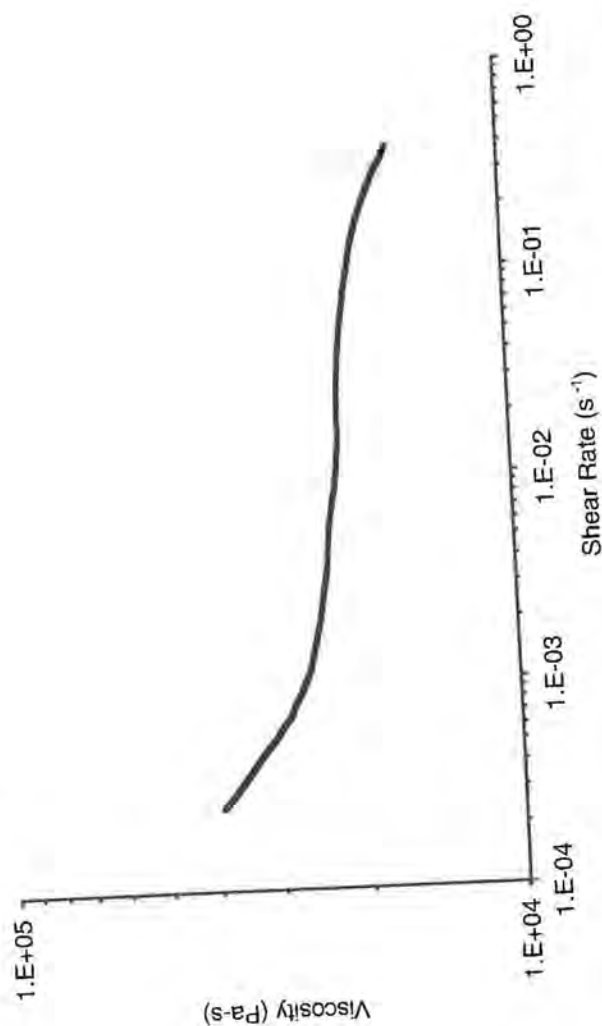


Figure 1.3 Parallel plate, continuous shear rheology curve for low-density polyethylene at 200 °C

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. As the 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

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

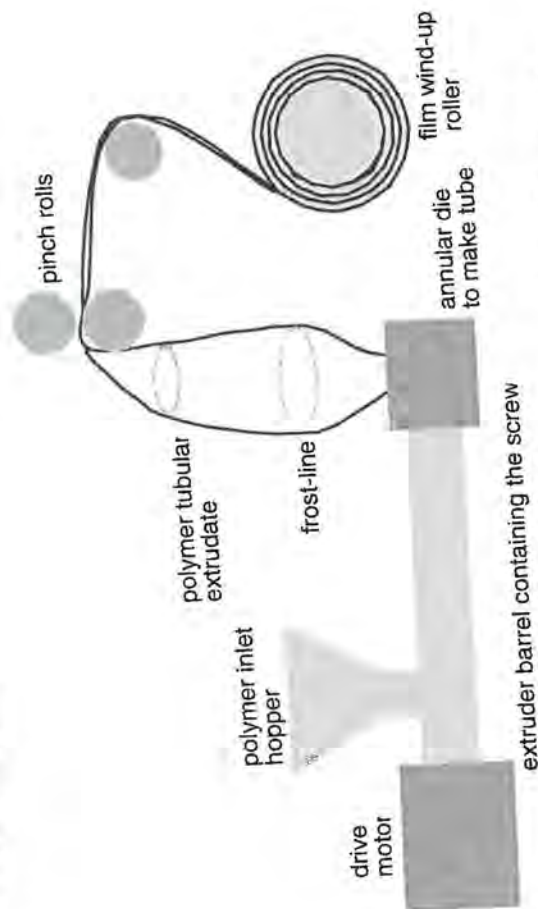


Figure 1.4 Diagram showing the extrusion blown film process

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].

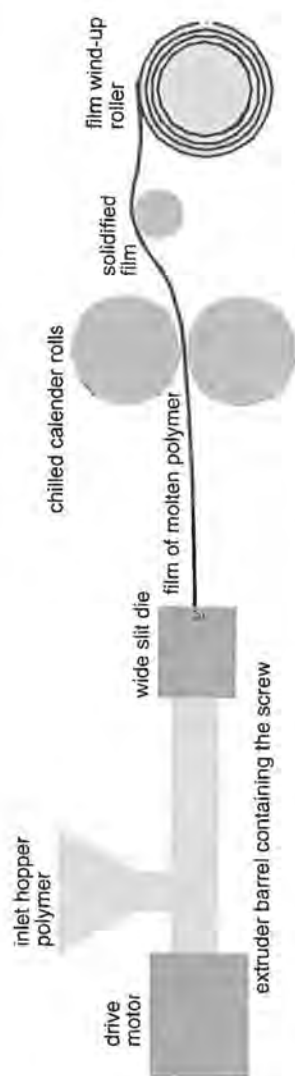


Figure 1.5 Diagram showing the extrusion cast film process with calendaring and extrusion coating

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 calendar 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 calendar 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].

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 calendar 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 calendar 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

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.

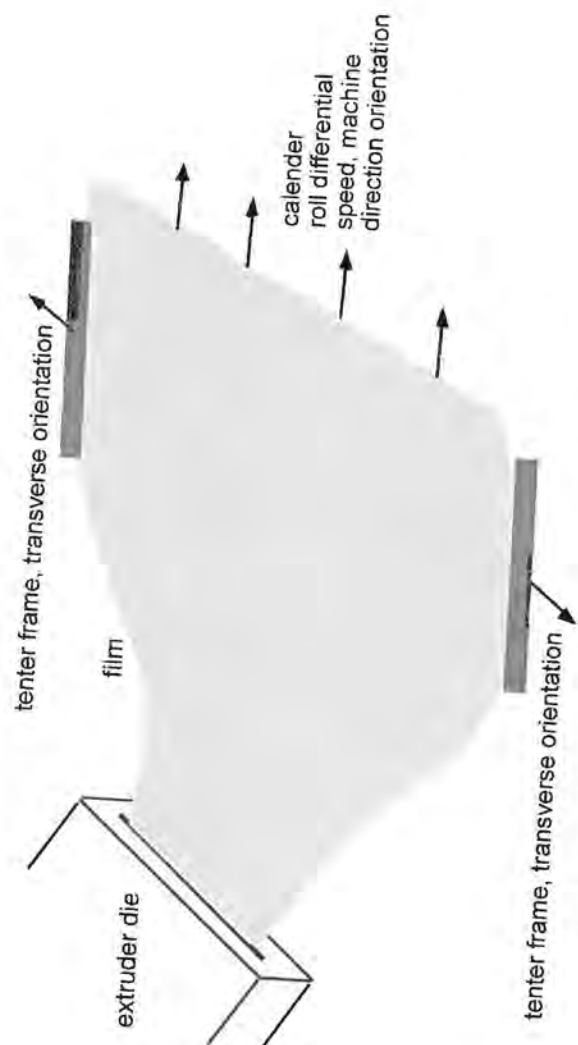


Figure 1.6 Schematic diagram for biaxial orientation of cast film

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

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

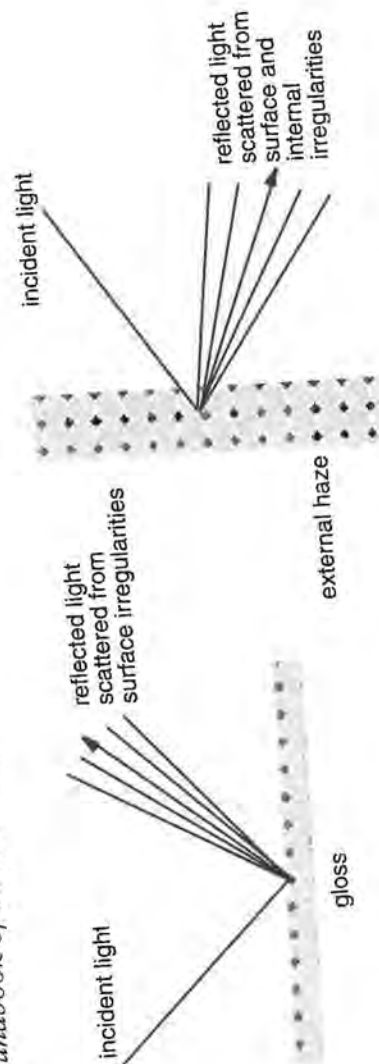


Figure 1.7 Diagram showing the origin of gloss and haze in polymer films

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

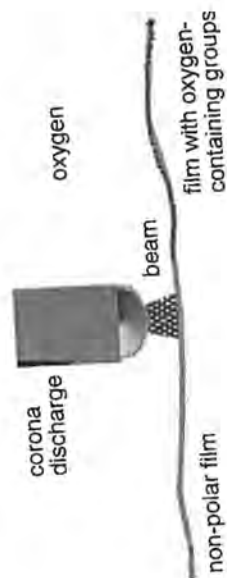


Figure 1.8 Corona discharge surface treatment system

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.

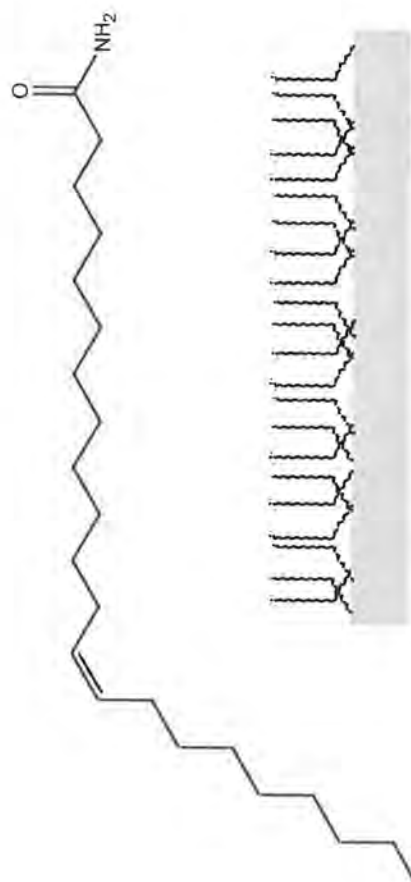


Figure 1.10 Structure of erucamide ($C_{21}H_{41}CONH_2$, *cis*-13-docosenamide) slip additive, and its mechanism for increasing slip. The diagram shows an array of erucamide molecules along the surface of a film, with the bent *cis* structure ensuring that they stay irregular

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

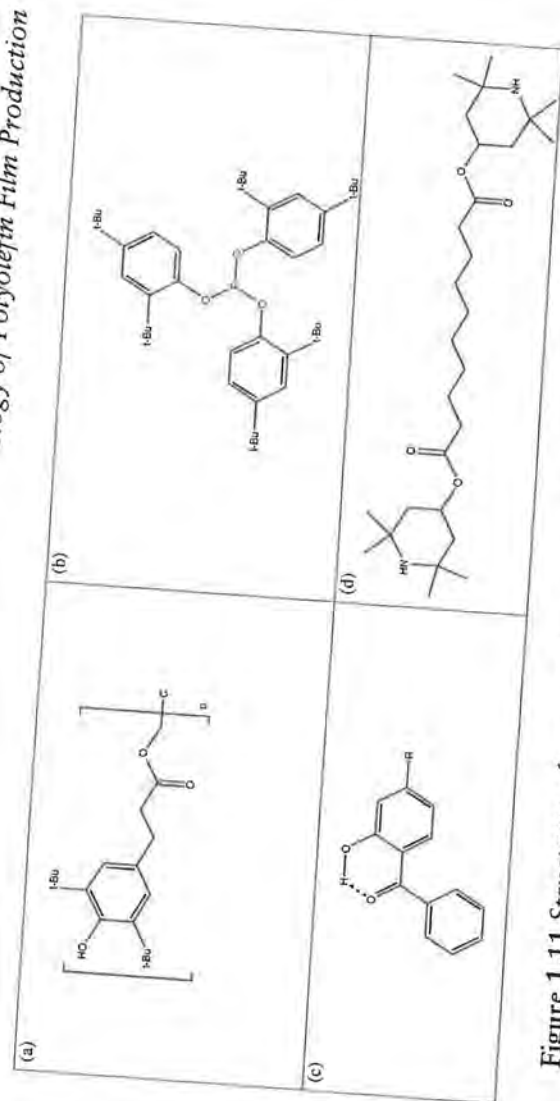


Figure 1.11 Structures of common heat and light stabilisers: (a) hindered phenol antioxidant; (b) tri(2,4-di-tert-butylphenyl) phosphite secondary antioxidant; (c) hydroxybenzophenone ultraviolet absorber; (d) hindered amine light stabiliser

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 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.

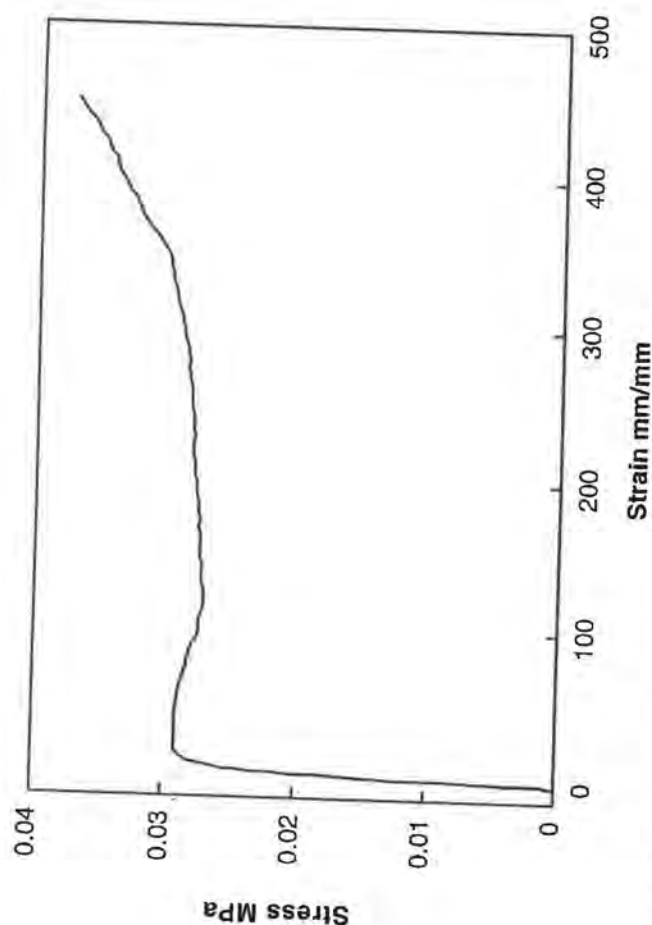


Figure 1.12 Stress-strain curve for linear low-density polyethylene showing the yield stress after the initial linear elastic region, then the strain-hardening region after 350% strain

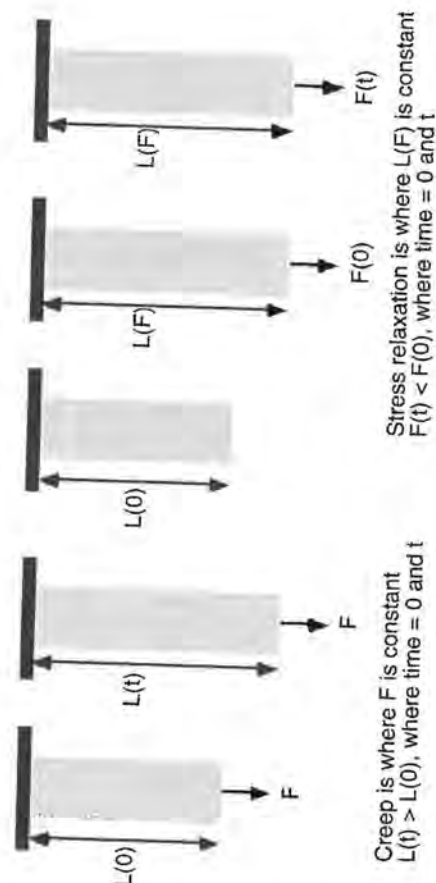


Figure 1.13 Schematic for the mechanism of creep and stress relaxation

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

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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.

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.

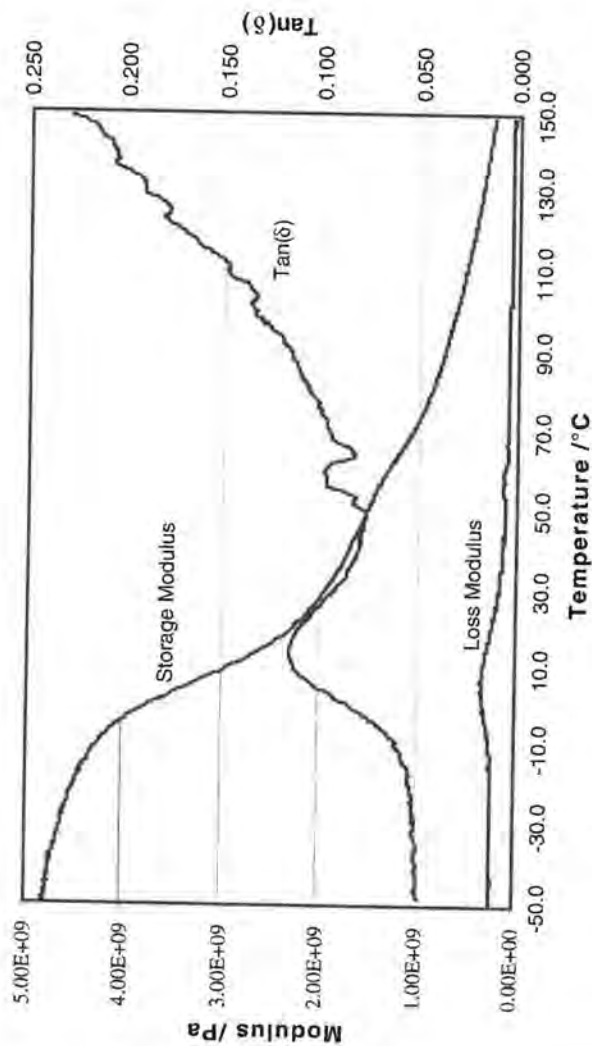


Figure 1.14 DMA curve for polypropylene, showing the storage modulus, E' , loss modulus, E'' , and damping factor, $\tan \delta$

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

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>I</i> = current <i>V</i> = voltage <i>f</i> = frequency <i>δ</i> = phase angle	$C = \frac{I \sin \delta}{V 2 \pi f}$
Conductance (<i>R</i>⁻¹)	$R^{-1} = \frac{I \cos \delta}{V}$
Permittivity (<i>ε</i>[']) <i>ε</i> ₀ = permittivity of a vacuum, <i>A</i> = area of electrode <i>D</i> = distance between electrodes	$\epsilon' = \left(\frac{C}{\epsilon_0} \right) \left(\frac{1}{A/D} \right)$
Loss factor (<i>ε</i>^{''}) <i>ω</i> = angular frequency <i>σ</i> = 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.

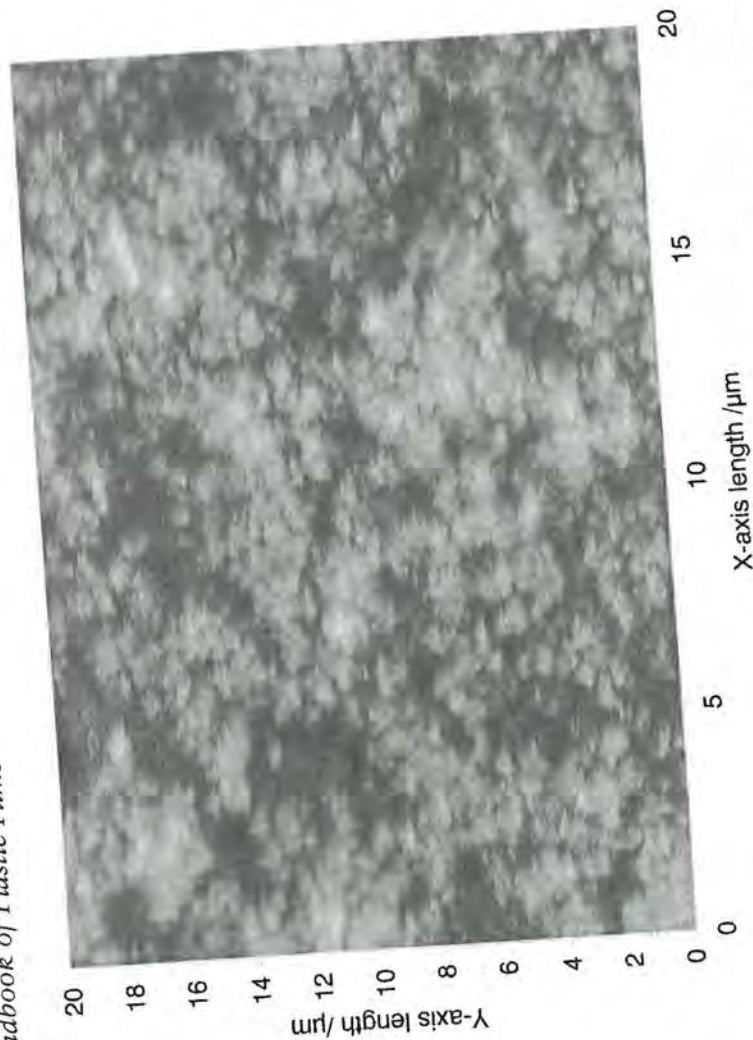


Figure 1.16 Atomic force microscope picture of the surface of linear low-density polyethylene film prepared by the extrusion blown film process

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

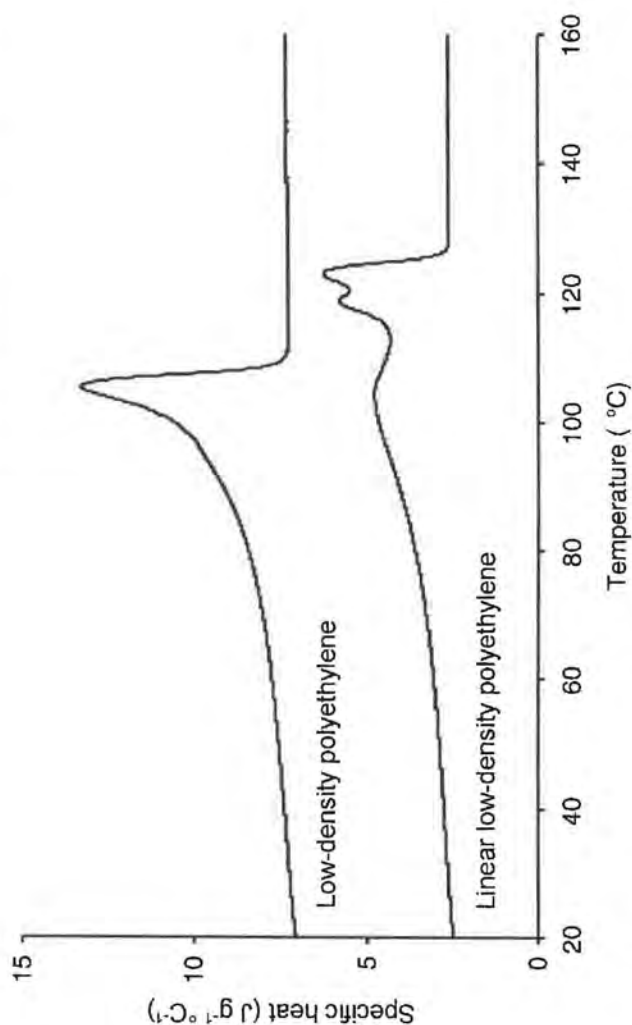


Figure 1.17 DSC curves for melting of linear low-density polyethylene and low-density polyethylene (for clarity, this curve has been shifted upwards by five units)

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

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

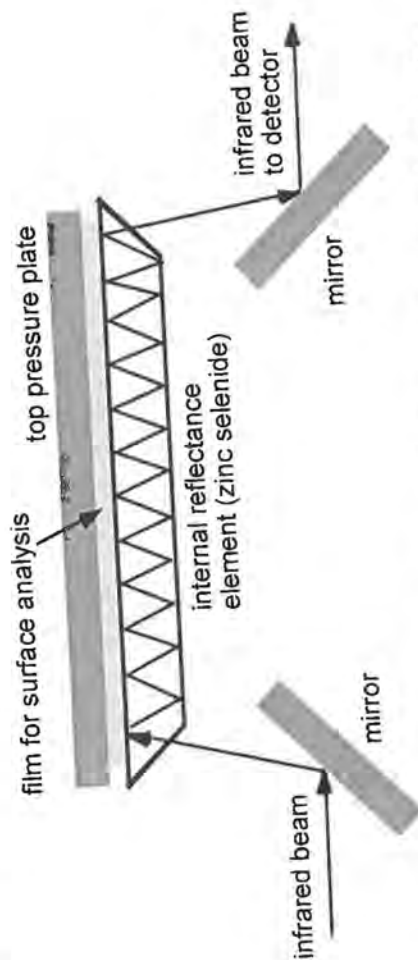


Figure 1.18 Apparatus for multiple internal reflectance (attenuated total reflectance) infrared spectroscopy for surface analysis of polymer films

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 $10\text{--}20 \mu\text{m}$ in thickness, and individual layers in multilayer films are often only $5 \mu\text{m}$ 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.

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.



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.

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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2 Processing of Polyethylene Films

Amin Al-Robaiddi

2.1 Introduction

A plastic is solid in its unprocessed and processed states. It is softened enough through the application of a combination of heat, pressure and mechanical working to be formed into a variety of shapes such as car bumpers, containers and plastic films. Most thermoplastic polymers are linear polymers. However, these chains twist and turn around to form a tangled structure [1].

Commodity polymers are low in cost and high in volume. They are used to a great extent in our day-to-day lives [2]. Worldwide usage is enormous and is increasing year by year. Rates of increase up to 5% per year are not unusual. Of these commodity polymers, polyolefins play the largest role, and therefore their production is of great importance. Polyolefins represent about 45% of total plastic usage: linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) make up 51% of total polyolefin use, the rest being 23% polypropylene (PP) and 26% high-density polyethylene (HDPE). In this chapter, some of the important properties, production techniques, and chemical and physical phenomena that are of interest for polyolefins will be explained.

Polyethylenes are made via free-radical and Ziegler-Natta (ZN) processes. The free-radical method, usually at high pressures (up to 3500 atm) and high temperatures (up to 300 °C), is the older of the two methods. The ZN processes usually have much milder conditions. Recent developments use metallocene catalysts to produce tailor-made polyolefins. The common means of distinction between the various types of polyethylene is by density. LDPE and LLDPE have a low density below 0.94 g/cm³, whereas that of HDPE is above 0.94 g/cm³. The density is influenced by polymer structure. The properties of each type are given in Chapter 1.

LLDPE for film application is characterised by the different processes used to produce the film and also by end-use application. The processes used to produce the film are determined by the molecular weight (molar mass) of the resin. For example, typical melt index ranges of 0.5-2 g/10 min are suitable for blown film, 2-6 g/10 min for slot cast film, and 5-12 g/10 min for extrusion coating.

for higher molecular weight resin, usually HDPE grades. The common flow index for all grades is the I_{21} (HLM1 = high-load melt index) measured at 190 °C and 3034 MPa.

In practical terms, the melt index is a guide to the relative level of properties of a material and the relative ease of flow that can be expected from the resin during fabrication [5, 6]. The melt index is inversely related to the molecular weight. As the molecular weight increases, the melt index decreases, and vice versa. Since the strength characteristics of polymers are related to the molecular weight, then melt index can be used as an indicator of polymer strength. With an increase in melt index, the tensile strength, tear strength, stress cracking resistance, heat resistance, weatherability, impact strength and shrinkage/warpage decrease. The modulus of rigidity remains relatively unaffected with melt index increase. For HDPE, the increase in melt index improves the gloss but has relatively little effect on transparency [4, 7]. With an increase in melt index, the ease of processing also increases if all other parameters (such as molecular weight distribution) are held constant.

2.2.2.1 Melt Flow Blend Relationship

It is often of interest to calculate the melt flow (MF) of a blend of resins whose individual MF values are all somewhat different. The literature contains a number of equations for calculating the viscosity of blends. When blending polyethylene resin, the most frequently used equation is the arithmetic average of the logarithms ($\ln$ or $\log$) of the melt indices, which is obtained as follows.

Given two polymers, A and B, of the same type and with weight-average molecular weights $M_w(A)$ and $M_w(B)$, respectively, the weight-average molecular weight of the mixture is defined as:

$$M_w(\text{mix}) = x_A M_w(A) + x_B M_w(B) \quad (2.1)$$

where x = weight fraction and so $x_A + x_B = 1$. Then the melt index equation for a blend of two samples A and B is given by:

$$\ln MI = x_A \ln MI_A + x_B \ln MI_B \quad (2.2)$$

The melt flow ratio can either be I_{21}/I_2 or I_{21}/I_5 , where the former is typical for injection moulding and low-density film grades and the latter is typical for higher molecular weight HDPE film, blow moulding and pipe grades. The melt flow ratio is a rough indicator of the molecular weight distribution and the shear-thinning characteristic of the polymer. The higher the melt flow ratio, the broader the expected molecular weight distribution, with the accompanying increases in shear-thinning behaviour. The melt flow ratio has a correlation with the molecular weight distribution, but it is not a purely linear relationship over a broad range [7-9].

A disadvantage of LLDPE resins is the need to modify existing and available extruders at the processor site to convert from LDPE to LLDPE products, because of the higher shear viscosity of LLDPE with narrow molecular weight (molar mass) distribution (MWD). Owing to its different shear and extensional rheology, LLDPE extrusion and processing conditions differ from those for LDPE. To optimise its processing, different screw designs have been developed and air rings have been modified according to the different extensional rheology.

2.2 Parameters Influencing Resin Basic Properties

Polyethylene resins are generally characterised by three parameters:

- (1) Molecular weight distribution (measure of processing ease and product properties),
- (2) Melt index (measure of molecular weight) and
- (3) Density (measure of branching or rigidity).

These three parameters are considered to be intrinsic properties of polyethylene. The following section discusses each of the basic parameters influencing resin properties.

2.2.1 Molecular Weight (Molar Mass) and Dispersity Index

In any polymer, there is a distribution of chain lengths or molecular weights. Accordingly, the molecular weight of polyethylene is not a uniquely defined quantity, but instead depends on what averaging formula is used. The reader is asked to consult any textbook on polymer science regarding this item [3, 4].

2.2.2 Melt Index (Flow Properties)

The melt index (MI) is an inverse measure of the length or average size of polyethylene chains. For a given class of polyethylene, MI can be used to estimate the molecular weight. By ASTM definition, the *melt index* is the weight of molten material (in grams) extruded in 10 min through an orifice at 190 °C under an applied stress of 2.16 kg, which means a stress of 303 kPa. Only under these conditions is the measurement defined as the melt index. Measurement under different loads is possible in connection with international standards, sometimes reported as I_2 (flow rate under specific load). Flow rates under defined loads and other conditions are referred to as flow indices. The common *flow index* measured at 190 °C and 690 kPa or I_5 (flow rate under a load of 5 kg) is used

2.2.3 Density

Density can be taken as a measure of the crystallinity of polyethylene. Since branching of the macromolecular chain affects the solid-state structure or crystallinity of polyethylene, density is also an indicator of chain branching. In this relation, we have to differentiate between short-chain branching (SCB) and long-chain branching (LCB). Long-chain branches are mainly present in LDPE, whereby short-chain branches predominate in HDPE and LLDPE. Polyethylene (PE) in its solid state is a semicrystalline material. To first approximation, its structure may be represented as a two-phase composite: a mixture of a hard crystalline phase (density ~1 g/cm³) and a soft noncrystalline amorphous phase (density ~0.84 g/cm³). The actual composite density depends on the relative amounts of crystalline and amorphous phases. Because short-chain branching disturbs the regularity of the PE chain, the crystallisation process is hindered and, accordingly, the crystallinity of the solid-state structure is reduced [9]. Thus, with increasing frequency of chain branching, the crystallinity and density decrease. HDPE, with little or no chain branching, has a density of approximately 0.94-0.97 g/cm³ and a crystallinity by weight in the range 60-85%. LDPE and LLDPE, with more and longer-chain branches, have a density of 0.9-0.93 g/cm³ and crystallinity by weight of 40-60%. The density range can be classified as shown below into four categories in accordance with ASTM D-1248 [10]:

- | | |
|---------------------------------|-------------------|
| (1) Type I (low density) | 0.910-0.925 g/cm³ |
| (2) Type II (medium density) | 0.926-0.940 g/cm³ |
| (3) Type III (high density) | 0.941-0.959 g/cm³ |
| (4) Type IV (very high density) | 0.960-0.995 g/cm³ |

Density is typically measured using a density gradient column. The specimen could be a pellet or a piece of a plaque produced under controlled cooling conditions. The rate of cooling affects the crystallinity, and this will affect the density. A plaque quenched in ice-water will have a lower density than a slowly cooled plaque. Boiling a slowly cooled plaque will increase the measured density. As a result of the faster cooling employed, a fabricated pellet will typically have a density (if unmodified by inorganic additives) lower than the ASTM density [9, 11].

The density measured is strongly affected by the addition of inorganic additives with higher density, such as antiblock agents for film-grade resins and other fillers. When blending materials, the specific volume should be arithmetically averaged:

$$1/\rho = x_1(1/\rho_1) + x_2(1/\rho_2) \tag{2.3}$$

where x is the weight fraction, ρ is density, and 1 and 2 represent samples 1 and 2.

For PE blends, since the densities are to some extent similar, arithmetically averaging the densities themselves is usually a good approximation. Increasing the density, with all other parameters held constant, will increase the shrinkage, modulus of elasticity, yield strength, heat resistance, gloss for HDPE, permeability resistance and hardness. An increase in density will increase the impact strength, stress cracking resistance, transparency and tear resistance. For HDPE resin, an increase in density will increase the tensile strength, and with increase in SCB, the tensile strength will be lower. Weatherability will remain relatively unaffected.

2.2.4 Chain Branching

Polyethylene produced with the high-pressure technology contains both long-chain branches (100-200 or more carbon atoms) and short-chain branches. Polyethylene produced with low-pressure technology has only short-chain branches (1-20 or so carbon atoms). The two types of branching have different effects. For example, LCB has a significant effect on melt rheological (flow) properties, whereas short-chain branching (SCB) has no measurable effects. These differences lead to the definitions of 'branched' PE, which contain LCB, and 'linear' PE, which essentially do not have any LCB. LCB affects the following melt flow properties:

- (1) Extensional viscosity ('strain hardening'),
- (2) Shear viscosity ('shear thinning') and
- (3) Elasticity (first normal stress differences).

LCB also affects the solid-state properties due to its influence on the melt flow properties. Owing to its tendency to strain-harden, the presence of LCB can lead to orientation effects, and those remain in the resultant solidified PE. This is seen in the blown film area. SCB, in contrast, has little effect on melt flow properties but plays a major role in the solid-state properties. SCB will affect the density, modulus of elasticity, heat of fusion, optical properties, impact resistance, tear resistance and melting point. While branch frequency (BF) is undoubtedly the most important SCB parameter, branch length and branch distribution also have important effects. It is well known that, at constant SCB frequency, the longer the branch, the lower the density. The density difference decreases as the density of PE approaches the HDPE region.

Homogeneous SCB in the situation in which the branch frequency is the same for all PE chains and, moreover, the branches are randomly distributed along the main chain.

Heterogeneous branching refers either to branch frequency varying from molecule to molecule or to a non-random distribution of branches along a given PE chain. At constant

overall branch frequency, the more heterogeneous the branching, the higher the density. In high-pressure PE, SCB is homogeneous while LCB increases as the molecular weight increases [9, 12].

This distribution can be measured by separating the polymer into fractions using chromatographic techniques. Temperature-rising elution fractionation (TREF) is a method widely used nowadays to determine the comonomer and branching distribution in polyolefins. The technique used to measure the distribution is carbon-13 nuclear magnetic resonance (^{13}C NMR). It gives the sequence distribution along the chain, but averages the distribution among chains.

SCB can be detected using Fourier transform infrared spectroscopy (FTIR) or ^{13}C NMR. SCB can be measured using three different units: frequency per 1000 backbone carbon atoms, weight per cent (wt%) or mole per cent (mol%). If SCB is reported in frequency per 1000 backbone carbon atoms, it can be converted using the fact that each monomer or comonomer contributes two carbon atoms to the backbone. Thus, there are 500 monomer/comonomer units making up the 1000 backbone carbon atoms.

2.2.5 Intrinsic Viscosity

The viscosity of a polymer solution or polymer melt, in general, is a measure of the fluid's resistance to flow. Intrinsic viscosity is a measure of the hydrodynamic volume of a polymer molecule in solution. It is sensitive to molecular weight conformation as well as molecular size [9, 12-16].

For a given set of polyethylene resins produced with the same process, intrinsic viscosity can be used as an indicator of the average molecular weight of the polymer. Because intrinsic viscosity is affected by molecular conformation, LDPE (with their long-chain branching) will assume a hydrodynamic volume in solution smaller than that of a linear PE of equivalent molecular weight. PE produced by different processes will have different linear relationships between $\ln(\text{melt index})$ and intrinsic viscosity. The molecular weight distribution may be a factor as well. The dilute solution viscosity test defines what is known as the viscosity-average molecular weight.

Intrinsic viscosity (dl/g) measurements are normally made by using a three-point zero-concentration extrapolation. Because it is a zero-concentration measurement, it is independent of concentration; the intrinsic viscosity is dependent on the solvent used in the test. Measurements of PE dilute solution viscosity have been made at 140 °C and at concentrations of 0.1, 0.2 and 0.3 g polymer/100 cm³ decalin.

More recent measurements have been made at temperatures higher than 140 °C with trichlorobenzene (TCB) at concentrations ranging from 0.025 up to 0.25 g polymer/100 ml solvent. The latter set of conditions (TCB, 140 °C) corresponds to the more typical size exclusion chromatography (SEC) conditions used to determine the molecular weight of PE.

2.2.6 Melting Point and Heat of Fusion

As the temperature rises from ambient temperature, the properties of a PE resin change from solid to viscous-like material. Some of these changes are due to facilitated plastic deformation of the crystalline phase. The most part, however, is due to melting of the crystalline phase.

The melting temperature of PE lamellar crystallites decreases as lamellar thickness decreases, or as crystallite internal perfection decreases (e.g., due to the partial incorporation of short branches). Since lamellae vary in thickness and perfection, the melting of PE occurs over a range of temperatures. The melting point of PE resin is to some extent a matter of definition. The most popular definition is in terms of a specified point on a differential scanning calorimeter (DSC) trace. The apparent melting point will vary with the method of measurement: mechanical response, dilatometer, X-ray scattering, light scattering or calorimetry. DSC is the most frequently used method for PE.

The apparent melting point decreases with increasing short-chain branch frequency (decreasing density), increasing short-chain branch homogeneity, decreasing crystallisation temperature (faster cooling) or decreasing short-chain branch length. In the first three cases, the effect is due to decreasing lamellar thickness. In the last case, the effect is due to decreasing internal perfection of the crystallites. In practical terms, the melting point can be used as an indicator of the density for a given PE type. While LDPE may have a melting point of ~120-127 °C, HDPE resins have melting points in the range of 129-135 °C.

The heat of fusion, ΔH_f , is the amount of energy required to accomplish the solid-to-melt phase transition. The heat of fusion is linearly proportional to the density. In theory, if the heat of fusion of 100% crystalline PE is known, the heat of fusion of the crystalline fraction of the PE sample can be determined by taking a ratio of the sample to 100% crystalline. In calculating the per cent crystallinity of a sample, a value (average of five literature values) of 68.4-69.2 cal/g (286.6-299.0 J/g) is used as the heat of fusion of 100% crystalline PE.

2.2.7 Melt Properties – Rheology

For convenience, flow can be classified into shear flow or extensional flow. Shear flows are those in which the velocity component varies only in a plane normal to its flow direction. Shear rheology plays an important role in PE extrusion. Extensional flow, in contrast, is characterised by a velocity component that varies only in its own flow direction. Elongational viscosity is important in film blowing, for example. It is generally not possible to predict the extensional rheology of polyethylene from its shear flow results or vice versa [9, 10]. The viscosity is reported versus either the shear rate or the extension rate.

2.2.7.1 Relation of Viscosity/Shear Rheology

In the melt of a high molecular weight polymer like PE, under equilibrium conditions, the chain molecules are not stretched out from chain end to chain end, but instead we assume the so-called 'random-coil' configuration, i.e., the contour of a chain resembles a three-dimensional random walk. The random-coil molecules are mutually interpenetrating, so that the environment of a given molecule consists mostly of segments of other molecules. These segments of other molecules collectively form a kind of 'tube' in which the molecule of interest is ensheathed. Flow of the polymer melt involves both the axial motion of molecules through their respective tubes ('reptation') and the lateral translation of the tubes themselves [7-9]. These processes obviously require the cooperative motion of large numbers of chain segments, which helps to explain why the viscosity (or resistance to flow) of polymer melts is orders of magnitude higher than that of small liquid molecules of similar chemistry.

Another difference between a polymer melt and a small liquid molecule is that the viscosity of PE melts depends on the flow rate [5, 6]. In particular, the shear viscosity of PE melts decreases with increasing shear rate, a phenomenon known as 'shear thinning'. Generally speaking, PE with a broad MWD shear-thins to a greater extent than PE with a narrow MWD. Shear thinning is of particular importance in the various extrusion processes (film, sheet, pipe, tubing, profile, blow moulding) as it permits easy flow through the extruder and die together with shape retention or sag resistance outside the die. Two polyethylenes that have the same melt index may be processed differently at the higher shear rates encountered in fabrication steps depending on their level of shear thinning.

PE viscosity decreases with increasing temperature or decreasing molecular weight. For linear PE over a wide range of MWD, the zero-shear viscosity (i.e., the shear viscosity at the limit of zero shear rate) is proportional to:

$$\exp(E/RT) M_w^{3.4}$$

where E is the flow activation energy (5-6 kcal/mol), R is the gas constant, T is absolute temperature and M_w is the weight-average molecular weight.

At constant MWD, the effect of increasing temperature or decreasing molecular weight is to shift the logarithmic viscosity versus shear rate vertically towards lower viscosities, and also horizontally towards higher shear rates [13-15]. The vertical shift is the same as for the zero-shear viscosities. For a temperature change, the horizontal shift has the same magnitude as the vertical shift. For a molecular weight change, the horizontal shift is usually smaller in magnitude than the vertical shift.

The zero-shear viscosity of branched PE is higher than that of linear PE at constant 'coil volume' (i.e., the spherical volume 'pervaded' by a random-coil molecule). This is easily understood in the light of the discussion of melt structure.

In the case of a branched PE molecule, the axial reptation of the main chain through its tube is necessarily coupled to the lateral translation of the side chains and their tubes [12]. The effect of this added constraint is to increase the viscosity over that of linear polymer. The viscosity of branched PE is also more sensitive to temperature than that of linear PE (apparent flow activation energy 10 kcal/mol versus 6-7 kcal/mol).

2.2.8 Elongational Viscosity

The rheological properties of PE in an elongational type of flow are very different from those in shear flow. This viscosity is measured under more of a 'tensile' mode. At particular elongation rates, the apparent elongational viscosity does not even reach a steady-state value within the time required to impose the desired total strain.

Furthermore, while the viscosity of narrow MWD linear PE resin may begin to level off within this time period, the viscosities of branched or very broad MWD linear PE resins often take a sharp upturn with increasing strain, similar to a rubber band, which becomes stiffer the more it is stretched [9, 17]. This phenomenon is known as 'strain hardening'. The rubber band analogy is a good one, because strain hardening is more an elastic phenomenon than a viscous one.

Strain hardening is observed more often for PE resin containing long-chain branching. It plays an important role in processes that involve highly elongational flows. In film extrusion, strain hardening limits the draw-down capability of branched or very broad MWD linear PE; however, it compensates by providing enhanced aerodynamic bubble stability in blown film. In extrusion coating and slot cast extrusion, strain hardening provides resistance to neck-in edge waver and draw resonance.

2.2.9 Elasticity

Polymer melts are, in general, viscoelastic. That is, regardless of the mode of deformation (shear or stretching) imposed on them, they exhibit both viscous and elastic properties.

The degree of viscous or elastic behaviour depends on the rate of imposed deformation and the temperature.

The molecules in a polyethylene melt can be considered as 'springs' that prefer a random conformation, but which, under an applied stress, can become uncoiled and extended. Thus, in a flowing melt, the molecules are partially uncoiled and extended in the direction of flow, thereby achieving a balance between the external stress driving the flow on the one hand and the retractive spring force on the other. Upon removal of the external stress, the melt will rebound as the molecules relax to their equilibrium random-coil conformation. The magnitude of this rebound or recoverable strain characterises the elasticity of the melt.

Melt elasticity increases with increasing flow stress, with increasing elongational component of the flow, with broadening MWD and with increasing long-chain branch content. With regard to the last two factors, elasticity is especially sensitive to the presence of a few large and/or highly branched molecules in the system.

The die swell percentage (ratio of diameter of extrudate/capillary die $\times 100\%$) is an indicator of the elasticity of the polymer melt after having been extruded through the capillary die. It is not the most accurate measurement, however, since it involves the physical measurement of the diameter of the extrudate. Elasticity determines the parison swell characteristics in blow moulding, and the warping characteristics in injection moulding. In PE film, heat shrinkability, optical clarity and mechanical anisotropy are directly or indirectly affected by elasticity.

2.3 Blown Film Extrusion (Tubular Film)

2.3.1 Introduction

The most widely used method for film extrusion is the tubular or blown film technique, which accounts for about 85% of all film production. Cast film extrusion is the other major process and accounts for about 10-12% of all polyethylene film extrusion [17]. These two methods (blown film and slot cast extrusion) are described in this section and the next.

2.3.2 Description of the Blown Film Process

To make polyethylene film, solid pellets are first dropped from a feed hopper into the extruder barrel, melted by subjecting them to heat and pressure, and the melt conveyed by

a rotating screw to the die. After having travelled all along the screw channel, the melt passes through a screen pack and supporting breaker plate and adapter into the die. The screen pack filters all contamination and foreign matter and removes them, before finally the melt is forced through the narrow slit of a die. The screen pack and breaker plate also help to increase the back-pressure in the barrel to improve mixing of the melt [18, 19]. The die might be straight or ring-shaped. The resulting thin film has the form of a tube or 'bubble'. Coming out of the extruder, the film is cooled and is finally rolled up on a core.

As the variety of polymers and blends has steadily increased, and film requirements have become more demanding, extruder and screw technologies have evolved to the point where screws are tailor-made for a specific system and application [19-22]. Figure 2.1 depicts a typical decreasing-pitch screw for LLDPE.

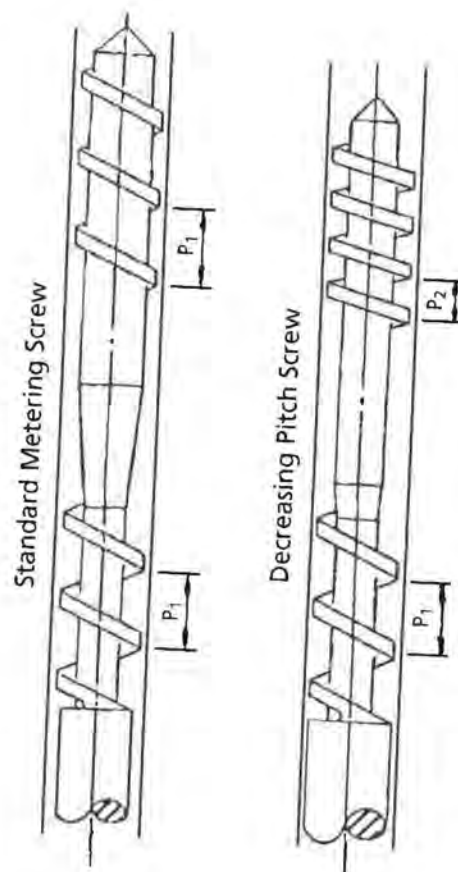


Figure 2.1 Typical decreasing-pitch polyethylene screw

In standard tubular blown film extrusion, the hopper feeds the resin to the screw, which conveys, compresses, shears, melts and pumps the material to the die. In tubular film extrusion, dies are circular in shape and are bottom or side fed (Figure 2.2).

2.3.3 Various Ways of Cooling the Film

The resin enters the die, flows around the core pin and exits as a thick-walled tube. While the resin is still in a molten state, air is introduced into the tube through a port in

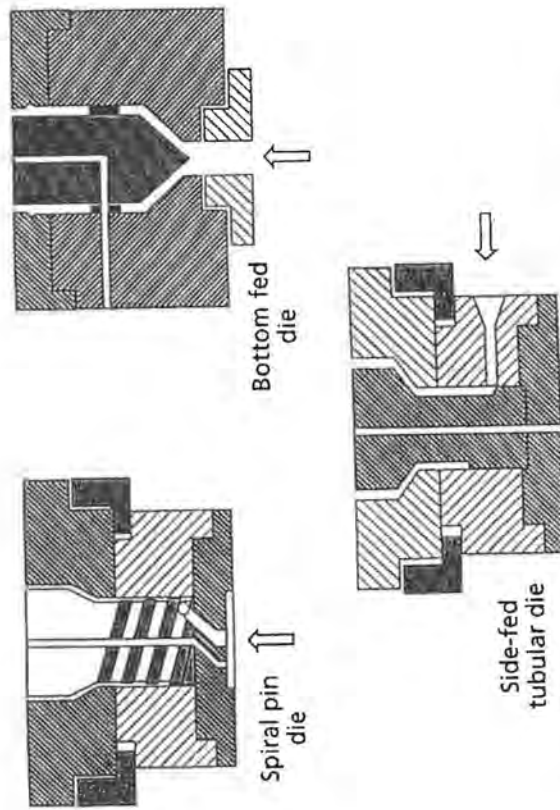


Figure 2.2 Blown film die in different arrangements

the centre of the die to expand the bubble to the desired diameter or lay-flat width. No additional air is required once the bubble diameter has been reached. By introducing air through the die-torpedo into the tube of film, the tube can be expanded to two or three times the diameter of the die. Thus, within limits, many different widths of film can be obtained from the same die. By varying the speed of the rollers closing the end of the bubble (the nip rollers), the amount of longitudinal stretching can be varied, and this is normally used to adjust the thickness of the film to the required value. This process has several advantages: With only one die, a range of film widths and thicknesses can be produced as well [23]. A bag can be produced by only one heat seal and two cuts, and very wide film can be produced (by slitting the tube) with equipment wide enough to handle only half this width. On the other hand, a drawback of the process is that the rate of cooling of the film is rather low, particularly if air cooling is used [23, 24]. At high output rates there are difficulties of controlling bubble movements sufficiently to keep film thickness between close limits. Further, because the film is nipped between two rollers at one end of the bubble, the film temperature at this point must be sufficiently low to prevent 'blocking'. The use of additives to prevent blocking can allow greater production speeds to be attained, and improvements in haul-off techniques have given better control over the swaying and shaking of the bubble.

The cooling rate is becoming the limiting factor on the whole process [25-27]. In this respect the process compares unfavourably with the slot-die process; also, with air cooling

it is not possible to use shock-cooling and high extrusion temperatures to effect a reduction in haze, as is possible with other processes.

The bubble might be externally cooled by means of an air ring encircling the base of the bubble. Cooling air is uniformly distributed and solidifies or quenches the tube. The collapsing frame serves to collapse the tube into a lay-flat (Figure 2.3), whereupon it enters the nip rolls for final flattening. The nip rolls seal the air in the bubble and draw the film upward from the die.

For given extruder output rate and blow-up ratio, the film gauge is controlled by the nip roll speed. It is desirable to have nip rolls of adjustable height to allow a lower die-to-nip distance than is normally used for LDPE extrusion [27]. The reduced height provides greater bubble support and stability, and allows the film to enter the nips when warm, minimising wrinkles from improper bubble geometry and/or melt temperature and gauge nonuniformity. Idler rolls guide the lay-flat from that point to the wind-up rolls, which wind the film on to cores.

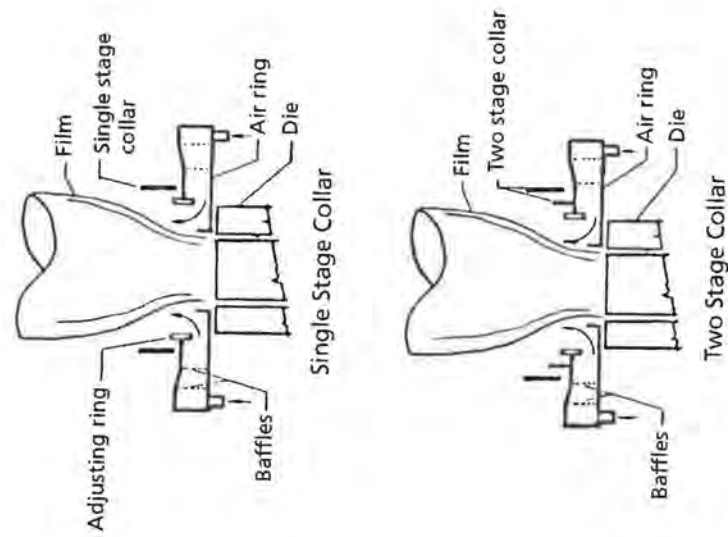


Figure 2.3 Air ring cooling the blown film

2.3.4 Extruder Size

In size, extruders are available from bench-top models for laboratory work up to 500 mm diameter screws. Screw sections and compression ratio have important functions. Commonly, the length-to-diameter ($L:D$) ratios of screws range from 15:1 up to 33:1. Recent developments consider a mixer at the screw end in the length range of 3D [27, 28]. A number of different mixers are available. The compression ratio is the ratio of the channel volume of one screw flight in the feed section to that in the metering section. A compression ratio of about 4:1 is recommended for film extrusion. High compression forces result in high internal heating, in good mixing of the melt and in pushing back any traces of air carried forward with the melt. Barrel diameter is determined primarily by desired output. Knowing the drive motor speed and the reducer ratio of a given extruder maximum rpm can be determined. Therefore, the throughput T for any given size extruder can be calculated, based on the following formulae (where D is the extruder diameter and h is the depth of the metering section):

(1) Neutral screw

- when D and h are in inches

(2.4)

$T = 1.15D^2h$ lb/h rpm

- when D and h are in millimetres

(2.5)

$T = 7 \times 10^{-5}D^2h$ kg/h rpm

(2) Controlled screw

- when D and h are in inches

(2.6)

$T = 1.4D^2h$ lb/h rpm

- when D and h are in millimetres

(2.7)

$T = 4.6 \times 10^{-5}D^2h$ kg/h rpm

Then it is easy to match dies and extruder capacities [28, 29]. Maximum extruder rpm can be calculated by dividing gear reduction into rated motor speed.

Some estimates of extruder size and die sizes based on throughput and cooling capacity are shown in Table 2.1.

Table 2.1 Some estimates of extruder size and die sizes based on throughput and cooling capacity

Extruder size		Die diameter	
inch	cm	inch	cm
1.5	3.81	up to 4	up to 10.16
2.5	6.35	6 to 12	15.2 to 30.5
3.5	8.89	12 to 18	30.5 to 45.7
4.5	11.43	18 to 28	45.7 to 71.1

2.3.5 Horsepower

The horsepower needed to drive the extruder motor is important. Based on a given pound per hour per horsepower (lb/h hp) relationship, the die, extruder and motor can be matched to give an optimum equipment arrangement. The examples in Section 2.3.6 give the pound per hour per horsepower values generally expected for 0.2 and 2.0 melt index resins extruded with neutral and water-cooled screws. Table 2.2 gives the normally supplied drive motor horsepower ratings for several extruder sizes.

Table 2.2 Extruder size versus horsepower relationships

Extruder size		Drive motor rating	
inch	cm	hp	kW
1.5	3.81	5 to 7.5	3.78 to 5.59
2.5	6.35	20 to 40	14.91 to 29.88
3.5	8.89	60 to 100	44.71 to 74.57
4.5	11.43	75 to 150	55.93 to 111.86

2.3.6 Selection of Extrusion Equipment

Selection of blown film equipment should be made in a logical sequence [28]. Before deciding on specific equipment, the type, size and end-use of the film to be produced should be determined. Knowing these variables, selection of proper equipment for a given application is fairly simple. Blow ratio is the tool by which the proper die size can be selected (Figure 2.4). In general, blow-up ratios of 1.5:1 to 3.5:1 are best suited for film production.

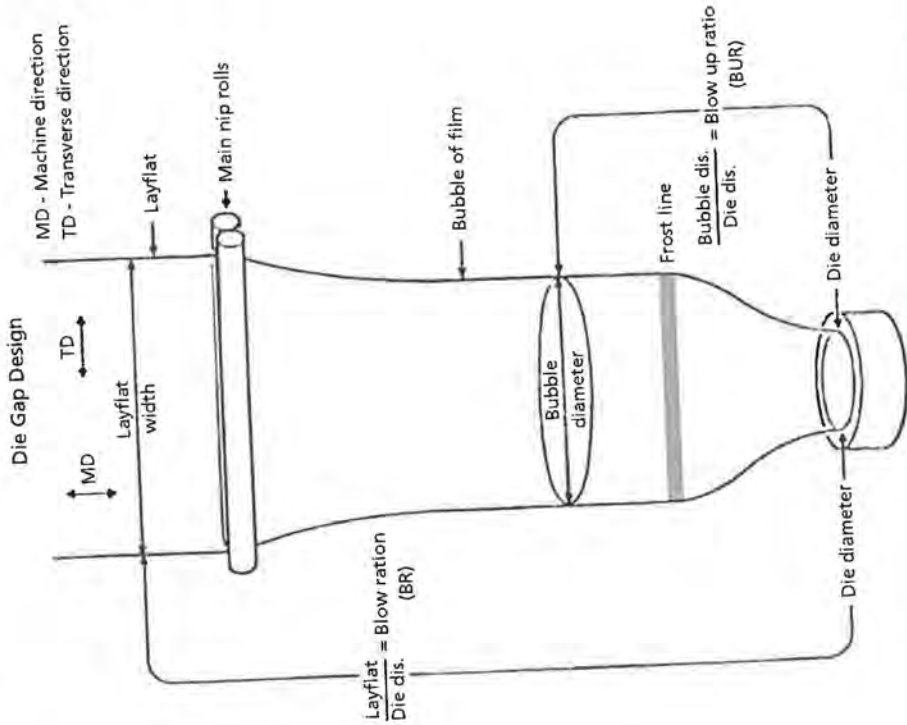


Figure 2.4 Schematic drawing of the blow ratio of film and the blown film width after the nip rolls have flattened the bubble to a double layer of film

Die size and cooling capacity are the major considerations in the selection of an extruder. The general 'rule of thumb' in the industry is to expect a throughput of 5-7 lb/h inch (0.9-1.2 kg/h cm) of die circumference. Die capacity and drive motor horsepower, which depend on several extruder size factors, can then be calculated. Some typical values are given in Table 2.3 and Table 2.4, respectively.

Table 2.3 Calculated die capacity depending on melt index and type of screw

Die diameter		Output	
inch	cm	lb/h	kg/h
4	10.16	75	34.0
6	15.24	110	49.9
8	20.32	150	68.0
10	25.40	190	86.2
12	30.48	220	99.8
16	40.64	300	136.1

Table 2.4 Drive motor horsepower depending on several extruder sizes

Melt index	Screw	Rate	
		lb/h hp	kg/h kW
2.0	Neutral	8 to 10	13.1 to 16.4
2.0	Cooled	5 to 6	8.2 to 9.8
0.2	Neutral	5 to 6	8.2 to 9.8
0.2	Cooled	3 to 4	9.9 to 6.6

2.4 Cast Film Extrusion

2.4.1 Description of the Cast Film Process

In cast film extrusion, the melt is forced through a flat or slotted die opening, either directly into a cooling water-bath, or tangentially contacting a highly polished, water-cooled chill roll (*cf.* Chapter 1). The flat film is cooled by two or more of these rolls and is carried by idlers to conventional treating and winding equipment. The film is stretched longitudinally between the die and the cooling-bath or rollers to the required thickness. Chilled steel rollers are preferred to a water-bath if the film contains hydrophilic materials such as antistatic agents, which cause some wetting of the film, with subsequent drying difficulties. Chilled rolls also allow greater production speeds than a water-bath [22, 25-27].

Flat film dies are often very long and heavy to install or to change [18]. Unfortunately, there is no close relation between die opening and film thickness. Generally, high gauges

require large openings. To produce a film of 2.5-27 μm thickness, the opening is normally around 0.5 mm. Usually one of the jaws is adjustable by means of screws so that the die opening can be reset, using a brass feeler gauge of known thickness and a torque wrench.

Die temperature and resin temperature at the die lands are usually higher than in blown film dies, ranging up to 300 °C. It is important to keep melt temperature uniform. The die always has a number of heating zones. To minimise temperature variation and fluctuations in film quality, the temperature along the die should be kept within very strict tolerances of 1 °C. To avoid film faults and imperfections, the inside die surface as well as the polishing rolls must be kept well polished. Slightly surface irregularities will result in gauge variations and die lines (lengthwise parallel grooves).

A regular die cleaning schedule will usually prevent faults in the inner surface. For the production of very thin films, an air knife is very commonly used. When the hot film is drawn down on to the first cooled chill roll, it may 'neck-in' (shrink) at the edges. Neck-in is the difference between the hot melt width at the die lips and the film width on the chill roll. When film with beading is wound up, the roll will sag in the middle, making it difficult to use it later for packaging or bag-making. Therefore, such a film must be trimmed at both edges.

Neck-in will not occur in blown film production, since the bubble has no edges that may shrink. Another cast film defect, which has something to do with cooling, is 'puckering' (a slight bulging across the film recurring at regular intervals). Running the first chill roll hot may reduce puckering. If the roll runs cold, the film may later warm up in storage and expand, and the roll may become loose. If the melt flows well, there is little danger of severe puckering.

The production of packaging bags from flat film requires special machinery to effect sealing of the sides of the bag as well as the bottom.

A considerable reduction in haze can be obtained by shock-cooling. This is not possible in the tubular film process except by friction contact with water-cooled metal, with the consequent marking of the film.

2.4.2 Effects of Extrusion Variables on Film Characteristics

2.4.2.1 Optical

Generally, with increased stock temperatures, higher gloss and lower haze will be obtained for low-density polyethylene. As the melt becomes hotter or more fluid, molecules will

have more time to align themselves and give a smooth film, which is a prerequisite for good gloss and low haze. Other problems such as bubble stability may result, however. In tubular extrusion of high-density polyethylene, the melt temperature increase has a minimal effect on the optical properties of the inherently hazy film [28-31]. When the blow-up ratio (BUR) is increased from 1.5:1 to 3:1, the gloss increases and the haze decreases in low-density polyethylene film, but the effect is negligible in high-density polyethylene film.

In slot casting and as is observed in tubular film extrusion, increasing the melt temperature generally improves optical properties, although the degree varies with various high-density polyethylene resins. Increasing film speed generally results in poorer optical properties – increased haze and lower gloss.

2.4.2.2 Haze

Haze may be of two kinds: surface roughness caused by melt flow phenomena, and surface roughness and internal optical irregularities caused by crystallisation. The faster the film cools between the extrusion die and the freezing point, the less is the haze resulting from crystallisation, and the greater is the haze resulting from flow. In high-density polyethylene, in which the haze caused by crystallinity is dominant, shock-cooling can be used to produce almost haze-free film.

Haze in film was formerly accepted as an unavoidable property of polyethylene, but it has been shown that commercially available polymers of slightly higher density than the normal 0.918 g/cm³ give film of lower haze. The higher density of these materials results in a greater susceptibility to 'brittle' tearing, other things being equal, and in greater gloss, clarity and stiffness.

In soft-goods packaging, haze in the film dulls the colour of the packaged article as seen through the film, and much of the sales appeal of using a transparent package is lost. Provided adequate toughness is retained, film of the lowest possible haze is required for this market.

2.4.2.3 Gloss

Since it has been found that small increases in the density of polymers could result in better gloss, the packaging market has demanded this property in order to add sparkle to the package. However, it has been suggested that too much gloss may destroy some of the appeal of a package by reflecting too much of the shop's lighting and of the variously

coloured goods in the vicinity. A reduction in chill roll temperature generally improves both haze and gloss in high-density polyethylene films.

2.4.2.4 Impact Strength

To have good impact strength, a balance of orientation between machine direction (MD) and transverse direction (TD) molecular structure is needed. Therefore, an increase in blow-up ratio tends to balance this orientation in both directions. As the stock temperature is increased, impact strength increases and a better balance of orientation (machine direction versus transverse direction) results. High-density polyethylene has a greater tendency than low-density polyethylene to orient and show large machine direction versus transverse direction differences, i.e., splittiness.

The toughness of film is its most important feature in the packaging of agricultural products (potatoes, carrots, etc.) and building applications. For these uses, the haziness of the film is not of great importance, and, as toughness and haze are to a certain extent mutually exclusive, hazy film has been accepted.

The tensile strength of the film is, as expected, mainly dependent on melt flow index, but the apparent brittleness depends mainly on the density of the polymer: the higher the density, the more brittle is the film. Brittleness also depends partly on the extrusion conditions of the film.

Brittleness of film should not be mistaken for the kind of brittleness encountered in mouldings. Examination of a 'brittle' tear does not show a sharp fracture but reveals a narrow edge of stretched film. A 'brittle' film requires much less energy to tear than does a 'non-brittle' one because a smaller area of film is stretched before the tear occurs. If the stretching is highly localised, a 'brittle' tear occurs; if the stretching is distributed over an area, a 'non-brittle' tear results. 'Brittle' tears are more likely to occur if the tearing stress is applied at high speed, such as in an impact, and film is normally tested under such conditions.

As the density of polyethylene increases, so also does its rigidity. Film made from HDPE is stiffer in both handling and appearance. In over-wrapping machines designed to handle stiff 'Cellophane' or paper, stiffness exceeding some minimum value may be essential.

Increasing the melt temperature in the slot casting process decreases tensile strength in the machine direction, but produces film with more balanced orientation and a resulting increase in impact strength. Impact strength is increased by a reduction in chill roll temperature in the slot casting process.

2.4.2.5 Blocking

Although blocking is not strictly a property of the film itself, it is one of the most serious limitations on the high-speed production of film by the blown extrusion process. For higher-density polymers, blocking is a less serious limitation, because the increased rigidity of the film prevents the intimate contact obtained between flexible films. In contrast, in low-density polyethylene extrusion, increased stock temperature can sometimes cause blocking. Excessive film temperature during the collapsing of the tube will cause the inside surfaces to stick together.

2.4.2.6 Bubble Stability

As the blow-up ratio increases, the blown tube becomes larger and nonuniformities in polymer flow from the die and cooling air are magnified. With increasing blow-up ratio, the increased surface area that results is more susceptible to draughts. These external forces tend to make the bubble waver and cause wrinkling and poor gauge.

2.4.3 Effect of Blow-up Ratio on Film Properties

2.4.3.1 Optical

Up to a certain point as the frost-line is increased, gloss increases and haze decreases. However, beyond this point, the gloss decreases and the haze increases. The increase in gloss and decrease in haze from increased frost-line height occur because the molecules tend to become better oriented and do not allow molecule 'ends' to protrude, which would give a 'rough' surface. Too long cooling time gives rise to internal haze inherent in polyethylene.

2.4.3.2 Impact Strength

Impact strength is associated with molecular orientation. Thus, on increasing frost-line height without increasing the blow-up ratio, the orientation in the machine direction increases. This 'one-direction' orientation allows the molecules to line up or orient, thereby producing a film that is 'splitty' and poor in impact strength.

2.4.3.3 Bubble Stability

Bubble stability can decrease as stock temperature is increased. Instability results when the bubble (hot melt) lacks stiffness to resist the forces exerted by the cooling air and draughts.

Increased frost-line height produces a tube with a longer length of molten or hot material. This soft material is very susceptible to wavering because of lack of strength, draughts or variables such as nonuniform cooling. In order to maintain the stable bubble necessary for good gauge, low frost-lines are desirable.

2.4.3.4 Puckering

Puckering is an expression used in the slot casting process. Puckering is caused by a nonuniform frost-line on the first chill roll, which produces density variations in the machine direction. These density differences cause length variations that appear as small bags, or puckers. Increasing the melt temperature decreases the tendency for puckering, while reduction in chill roll temperature increases the puckering tendency [32, 33].

The draw distance (distance between die and chill roll) affects the film properties. Optimum draw distance for good film production varies with equipment size and production rates, and must be found experimentally. In general, optimum draw distances may range from 1-2 inch (2.54-5.08 cm) in laboratory equipment to over 12 inch (30.48 cm) in commercial equipment.

2.5 Processing Troubleshooting Guidelines

Economical film-making means the production of high-quality film in long trouble-free runs at the highest possible production rate. Since certain changes in machine conditions may improve quality while decreasing output, or *vice versa*, it is frequently necessary to find some kind of compromise between the two goals – high output and superior quality. In Table 2.5 some guidelines are given for machine operators to check their machine(s) and product(s) periodically to prevent unnecessary trouble during film production.

2.6 Shrink Film

Shrink-wrapping use is growing very fast worldwide and especially in Europe, both for light/small articles and for heavy/huge pallets. Low-cost polyethylene shrink film is produced on conventional equipment, by the blown extrusion process. No additional machinery is needed. Only processing conditions and resin characteristics need to be properly selected, according to the film's application. The film shrinks because a high degree of molecular orientation or internal stress was introduced into it during its manufacture. These stresses are 'frozen' in the film by the air cooling. When the film is

Table 2.5 Processing troubleshooting guidelines	
Problem	Possible cause and/or solution
Poor gauge	1. Poor die and/or air ring design
	2. Die and/or air ring need adjustment
	3. Air draughts
	4. Dirt in air ring
	5. Temperature or resin change
Poor optics	1. Improper resin for property desired
	2. Raise extrusion and die temperatures
	3. Raise frost-line height
	4. Increase blow-up ratio (2, 3, 4 can only be accomplished within limits of bubble stability and blocking)
Wrinkles	1. Poor gauge control
	2. Misaligned rolls or collapsing tent
	3. Air draughts
	4. Unsupported film length too great
	5. Too much static build-up in film; use static eliminators
	6. Film slip is too low
	7. Film too stiff
	8. Keep a level frost-line
Blocking	1. Lower melt temperature
	2. Reduce cooling air temperature
	3. Increase air flow
	4. Increase distance from die to pinch roll if possible
	5. Use additional cooling rings
	6. Reduce primary nip roll pressure
	7. Reduce take-off speed
	8. Treatment too high
	9. Wind-up tension too high
	10. Improve air circulation in area of nip rolls
	11. Resin may need more antiblock
Low impact	1. Is the correct resin being used
	2. Increase blow-up ratio
	3. Lower melt temperature
	4. Lower frost-line height
	5. Reduce die opening
	6. Eliminate die and weld lines

Table 2.5 Processing troubleshooting guidelines <i>continued</i>	
Problem	Possible cause and/or solution
Low impact	7. Too high nip roll pressure results in weak crease strength
	8. Check gauges for low caliper spots
	9. Nip rolls may get too hot
	10. Eliminate scratches on film surfaces from collapsing frame, gussets and rollers
Film imperfections (holes, tear-offs, tube collapse, apple sauce, fish eyes)	1. Dirty screens and/or die
	2. Excessive gels in resin
	3. Melt either too hot or too cold
	4. Improper resin for draw-down required
	5. Decrease die opening for improved draw-down
	6. Improve homogenisation by greater back-pressure to screw
	7. Use water cooling of screw for improved resin homogenisation
	8. Improve gauge control
	9. Keep resin and scrap clean
	10. Check die land surfaces for imperfections
Bouncing	1. Frost-line too high or too low
	2. Melt temperature too high or too low
	3. Take-off too slow
	4. Extruder surging
	5. Improper adjustment of air flow from air ring
	6. Guide bars too tight
Bubble diameter control	1. Nip rolls not completely closed
	2. Nip rolls worn unevenly
	3. Air pressure to nip not holding
	4. Small pinholes in film
	5. Frost-line height change due to melts and/or air temperature change
	6. Frost-line height change due to change in air flow from air ring
	7. Air leakage into bubble because of leaking valve
	8. Air leakage in air lines leading into die for bubble diameter control
	9. Extruder surging
Poor roll flatness	1. Die and air ring should be rotating or oscillating
	2. Cores should not be out-of-round
	3. Eliminate stray air currents around bubble
	4. Eliminate wrinkles in film at wind-up
	5. Poor gauge control
	6. Film temperature at wind-up too hot, resulting in crushed cores

Table 2.5 Processing troubleshooting guidelines <i>continued</i>	
Problem	Possible cause and/or solution
Drop in roll weight	1. Screens becoming clogged
	2. Screw water temperature getting lower
	3. Flow of water to screw greater
	4. Feed hopper beginning to bridge
	5. Take-off speed has increased
	6. Pre-matted polymer in feed section of screw
Insufficient treatment	1. Take-off speed too great for treater setting
	2. Treater setting too low
	3. Gap setting between electrode and treater roll too great
	4. Dielectric roll (Mylar, Hypalon, etc.), has pinholes or is too thick
	5. Tune the treating unit
	6. Treater bar has too sharp edge
	7. Check for proper spark gap
	8. Check ink batch and how it is being used
	9. Resin may have too much slip
Overtreatment	1. Reduce treater setting
	2. Film not laying flat on treater roll
	3. Dielectric is loose (Mylar)
	4. Gap setting between electrode and treating rolls too small

reheated to a temperature above its softening point (such as in a shrink-tunnel or oven), the molecules tend to revert to their entangled unstrained state. Thus, the internal stresses are released, causing the film to shrink.

2.6.1 Shrink Film Types

Two shrink film types are mostly used today (Table 2.6). At present, bi-oriented shrink film is more popular than mono-oriented film. In the future, mono-oriented film is expected to make major gains in the total pallet-wrapping and sleeve-wrapping business. Bi-oriented film will remain for full overwrap of small and medium-sized packages. The most widely used film thicknesses are:

- 25-50 µm (thin shrink film) and
- 57-150 µm (heavy-duty shrink film).

Table 2.6 Shrinkage (%) of the two major shrink film types		
Type	MD	TD
Mono-oriented	60-80	10-20
Bi-oriented	50-60	30-50

2.6.2 Shrink Film Properties

The properties that fully describe a shrink film are the following:

- (1) Thickness and thickness uniformity,
- (2) Percent shrinkage (MD, TD),
- (3) Shrink strength (MD, TD),
- (4) Tear resistance (Elmendorf),
- (5) Impact strength (dart drop),
- (6) Puncture resistance,
- (7) Clarity (haze, gloss),
- (8) Slip and antiblock, and
- (9) UV resistance.

Normally a given application needs only some of these properties to be checked. Two examples are shown in Table 2.7.

Table 2.7 Shrink film properties to be checked according to application	
Display packaging of light articles, with sharp corners	Wrapping of heavy pallets, to be stored in the open air
Thickness	Thickness and thickness uniformity
Percent shrinkage	Percent shrinkage
Clarity	Shrink strength
Puncture resistance	Impact strength
Tear resistance	UV resistance

2.6.3 The Manufacture of Shrink Film

To produce film shrinkable in a given direction, molecular chains must be oriented in the same direction by processing. This orientation is obtained by stretching the film in the required direction. The greater the film stretching, the higher the molecular orientation and hence the shrinkage.

Every blown polyethylene film is shrinkable in the machine direction (MD), because it is normally stretched much more in this direction. In fact, from Figure 2.5 it can be seen that a film tube having diameter D_1 , length L_1 and thickness T_1 , in the molten state, is blown into a film tube having diameter D_2 , length L_2 and thickness T_2 , in the solid state, at room temperature.

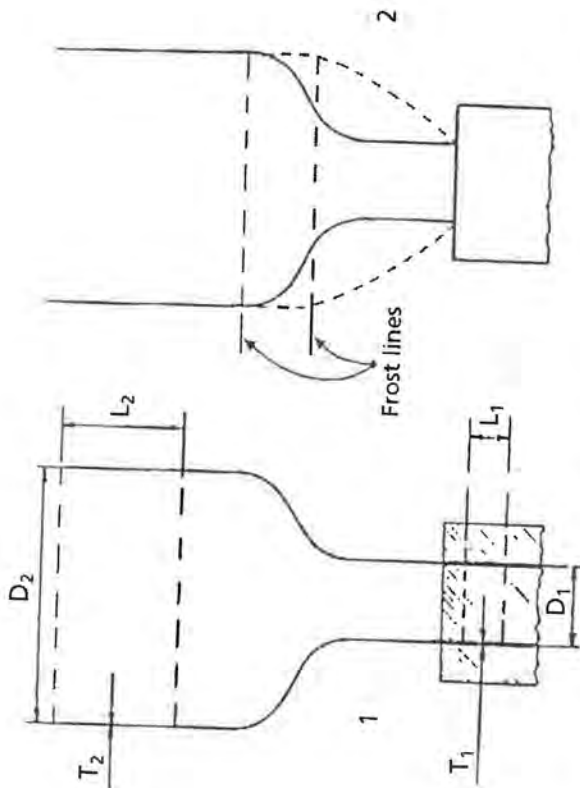


Figure 2.5 Frost-line and blow-up ratio (BUR) in shrink film

These two film tubes must have the same mass. This condition may be written as

$$\rho_2 \pi D_2 T_2 L_2 = \rho_1 \pi D_1 T_1 L_1 \tag{2.8}$$

where ρ_1 and ρ_2 are the film densities at the relative points. These densities are different due to the different film temperatures and pressures.

A normal thin blown film can be stretched to about 9:1 in the machine direction and to only 2:1 in the transverse direction. For this reason such a film will shrink very much in MD and almost nothing in TD. This means that this film is a mono-oriented type shrink film. Usually a thin shrink film is required to be bi-oriented, i.e., with more balanced shrinkage. This condition is achieved by properly regulating the processing conditions shown in Table 2.8.

Table 2.8 Influence of the processing conditions on the shrink properties of LDPE			
	Shrinkage		Shrink force
	MD	TD	MD TD
Stronger orientation in the machine direction	●	○	● ○
Larger BUR	○	●	○ ●
Higher take-off speed	●●●	○○○	●●● ○○○
Neck-type bubble shape		●	●●●
Higher frost-line	○○○	●	●●●
Production speed	●●●	○○○	●●● ○○○
Larger die gap speed	●●●		●●●
Larger length of die gap	○○○		○○○
Thicker film	○○○		○○○
Higher melt temperature	○○○	○○○	○○○ ○○○
Higher melt index	○○○	○○○	○○○ ○○○
●●● Strong increase			
● Little increase			
○ Fair decrease			
○○○ Strong decrease			

To obtain a balanced shrink film, the same amount of molecular orientation must be produced in both MD and TD. First, the stretching ratio in the machine direction (MDSR) and the blow-up ratio (BUR), in other words, the stretching ratio in the transverse direction, should be made equal. This corresponds to putting MDSR = BUR.

In practice, the stretching in the machine direction (MD) predominates, due to other factors (shearing suffered by the melt during its passage through the die, bubble shape,

etc.). Thus, the BUR needed to obtain balanced shrinkage is somewhat higher than the theoretical value. This corresponds to assuming a slightly higher coefficient (1.1 to 1.2) in the practical formula for balanced shrinkage.

2.6.3.1 Bubble Shape and Frost-Line

Bubble shape and frost-line are important parameters controlling the shrinkages in TD and MD. Referring to Figure 2.5, two types of bubble shape can be seen: one with a long neck (continuous line), corresponding to a higher frost-line; the other with no neck (dotted line), corresponding to a lower frost-line. The shape with a long neck gives more balanced shrinkages. This is easy to explain. In fact, for bubbles of this shape, transverse stretching predominates just below the frost-line, where the film is frozen, and no further relaxation can take place. Thus, a high level of molecular orientation in TD is retained in the film.

2.6.3.2 Resin Melt Index

Melt index has a remarkable effect on shrink strength and a slight effect on per cent TD shrinkage and on BUR for balanced shrinkages. In particular, the lower the MI, the higher the shrink strength. This means that for heavy-duty shrink film a low MI is preferred. Also, a low MI corresponds to lower BUR for balanced shrinkage and to higher TD shrinkage.

The MWD has only a slight effect on shrink temperature. In particular, a film obtained from a resin with narrow MWD (or low swell) shrinks at lower tunnel temperatures. The presence of slip and antiblock additives has no effect on film shrinkage.

Ethylene-vinyl acetate copolymers (EVA) with low vinyl acetate (VA) content give shrink films having the following properties:

- (1) Faster shrinkage (higher tunnel production),
- (2) Lower shrink temperature,
- (3) Higher impact resistance (at low temperature),
- (4) Higher puncture resistance,
- (5) Lower slip and antiblock, and
- (6) Higher gas/moisture permeability.

These films find application both for light shrink-wrapping and for heavy pallet wrapping.

UV stabilisers are necessary for applications in which the wrapped item (usually a pallet) is stored in the open air. Stabilisers have no effect on shrinkage. They only affect shrink film prices.

2.6.4 Shrink Tunnels and Ovens

The shrink-wrapping technique consists of wrapping and heat-sealing the article loosely in the film. The loose film perimeter should exceed the article's perimeter by no more than 7-10%. The package is then conveyed through a shrink tunnel or into an oven. Many types of heating system are used, the best being that using hot circulating air, because it gives more uniform heating. The most important properties of a shrink film from the point of view of an end-user are the following:

- (1) Percent shrinkage (MD, TD),
- (2) Shrink strength (MD, TD),
- (3) Shrink speed and
- (4) Shrink temperature.

The last two depend on film thickness and on the nature of item to be packed. In fact, both these factors affect the amount of heat required to reach the softening point of the film. Finally, it is worth pointing out that the maximum shrink strength is reached when the film cools outside the oven and not inside. In fact, inside the oven the film shrinks with a small shrink force, because it is hot and soft. When it cools rapidly to room temperature outside the oven, the film shrinks tightly around the article, with a much higher shrink force.

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3 Processing Conditions and Durability of Polypropylene Films

H. Aglan and Y.X. Gan

3.1 Introduction

The durability of polypropylene (PP) films under tensile loadings and ultraviolet (UV) irradiation is a very important end-use property. In this chapter, an overview of the structures, synthesis, processing and applications of semicrystalline PP films is introduced. The UV degradation mechanisms and the effect of UV degradation on the durability of PP films are then presented. The functions of different additives in PP films are described. Research findings based on a case study of the durability of several groups of PP films with additives such as UV stabilisers, antioxidants and colouring pigments, (e.g. calcium carbonate), are summarised. In the case study, typical PP film specimens taken from different processing stages are tested to establish the effect of composition and processing conditions on the durability of PP films. Microstructural features of the films are identified and correlated with their durability. It has been found that a lack of proper addition of UV stabiliser and antioxidant agent severely degrades the durability of PP products. UV-degraded PP woven fabrics made from stretched PP films totally lost their load-bearing capability and displayed severely damaged structure with extensive microcracks, voids and dispersed secondary particles. It has also been found that unstretched PP materials have very good durability under static tensile loading. The stress-strain behaviour shows several distinct deformation stages: elastic deformation, yielding and cold flow followed by strain strengthening. The stress-strain relationship of stretched PP films reveals an elastic deformation stage followed by limited plastic deformation from which no obvious cold flow was found. However, stretching results in the drastic decrease in durability of these films. The durability of the stretched films is less than 70%, while before stretching it was about 600%. Calcium carbonate pigment causes a decrease in tensile strength of stretched PP tape, while UV stabiliser does not change the strength and durability of PP films appreciably. A study of the surface morphology of these PP film samples revealed a similar smooth surface with unidirectional texture. Defects in the form of crevices, grooves and intruded particles were found on the surface of PP films with calcium carbonate colouring pigment.

PP is a thermoplastic polyolefin polymer [1]. The structure of PP is stereoregular [2-5]. Crystalline PP was invented in the early 1950s by independent groups in the USA and

9 Applications of Plastic Films in Packaging

Susan E. Selke

9.1 Introduction

Nearly all products are packaged at some point in their life-cycle. Plastic films are widely used in packaging, and continue to grow in use as more and more applications switch from rigid to flexible packages. Flexible packages generally take up much less space than the rigid structures they replace, especially before they are filled with product. They commonly require less material, as well. Therefore, switching from rigid to flexible packaging can provide significant economic savings in warehouse space and transportation, as well as in package cost. On the other hand, because flexible packaging does not usually have as much strength as rigid packaging, stronger distribution packaging may be required. Opening and reclosing of flexible packaging may also be less user-friendly, and consumers may perceive some types of products in flexible packaging as being lower in quality than equivalent products in rigid or semi-rigid packages.

Common flexible packaging forms include wraps, bags and pouches. In these packages, plastic films may be used alone or combined with paper and/or metal to serve the basic packaging functions of containment, protection, communication and utility in the delivery of quality products to the consumer. While plastic films are most often found in flexible package structures, they may also be used as a component in rigid or semi-rigid package structures, for example, as a liner inside a carton, or as lidding on a cup or tray.

The most common film used in packaging is low-density polyethylene (LDPE), defined broadly to include linear low-density polyethylene (LLDPE). Appreciable amounts of high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polyamide (Nylon) and other plastics are also used

9.2 Packaging Functions

Before examining applications of plastic films in packaging, it is useful to take a moment to consider why we use packages at all, since that will help in evaluation of the advantages and disadvantages of plastic films as packaging materials. The functions of packaging can be described in many ways. One simple way of organising them is to consider the basic packaging functions as containment, protection, communication and utility.

The containment function of packaging is the most basic. Many types of goods cannot be readily moved from one place to another unless they are contained in some manner. This is obvious for liquids and gases, but is also true for many small solid items, for example, marbles, nails, laundry detergent powder and potato chips (crisps). The package confines these items in a way that makes it feasible to transport them.

Sometimes the containment function is considered part of the more inclusive protection function of packaging. An important attribute of many forms of packaging is the ability of the package to protect the product from some type of damage associated with its interaction with the environment. In the example above, the marbles and nails must be protected against exposure to dust and dirt to remain in a condition that will permit their sale. The laundry detergent needs to be protected from exposure to excess moisture that could cause caking. The potato chips must be protected against light and oxygen, which can cause rancidity. In some cases, protection of the environment from the product is provided by the package. A water-soluble pouch for agricultural chemicals has, as its prime function, protection of the user from exposure to the hazardous undiluted chemical.

Packages also serve as a vehicle for communication. In most cases, the package must in some way communicate what it contains. Sometimes this is as simple as being transparent, so that the user can see what is inside. Since the package is often the primary sales tool, however, communication needs are usually much more extensive. The package must not only communicate what is inside, but also act to convince the potential consumer to purchase the product. Often, there are a number of legally required communications, such as the amount of product, where and by whom the product is made, required warnings, etc.

Packages also provide utility, either for the end-user or for others who interact with the package along the supply chain. Utility includes attributes such as a tear strip for opening and tamper evidence, a zipper closure for resealing, and a hole for use in hanging the packages on a display.

Individual packages or package elements often provide more than one function, simultaneously. For example, a stand-up pouch for snack foods provides: containment; protection of the product against oxygen and moisture; communication of identification, legally required, and sales messages; opening and reclosure features for consumer utility; and the ability to stand conveniently on the retailer's shelf and present a reasonably flat front panel to catch the consumer's eye.

9.3 Flexible Package Forms

Flexible packages come in two basic forms: wraps, and bags or pouches. A wrap consists of plastic film that has not been formed into a package shape. The film is simply wound around

the product or products to be contained, and held in place in some fashion. In a bag or pouch, some shaping of the plastic is done, either before or at the same time as the product is added. Most often, this shaping is done by heat-sealing the edges of the plastic together.

9.3.1 Wraps

9.3.1.1 Stretch-Wrap

One of the largest uses of plastic films in packaging is in stretch-wrap used for bundling pallet-loads of products together, in order to unitise them for distribution. The plastic film, most often linear low-density polyethylene, is stretched as it is wound around the products and pallet, usually in a spiral fashion. When enough has been applied, the film is cut, and the tail of the film is adhered to the load, usually by self-cling. When the stretching force is released, the film's tendency to return to its unstretched dimensions causes a restraining force to be exerted on the load, thus unitising it and keeping it from shifting when the load is moved during distribution.

In addition to its unitising function, stretch-wrap also protects the load against moisture, dust and abrasion. Stretch-wrap can also be used to provide this protection to single items, or to unitise smaller than pallet-load quantities of goods.

While stretch-wrap is simple in conception, it may have a fairly complex structure. It is desirable for each layer of stretch-wrap to stick to the layers below, but it is undesirable for adjacent shrink-wrapped loads to stick to each other, or to other things with which they come in contact. Therefore, the stretch-wrap may have a multilayer structure, with tackifying agents added to the inside layer to enhance cling. Low-density polyethylene, polyvinyl chloride, ethylene-vinyl acetate and other polymers are used as stretch films, in addition to LLDPE.

9.3.1.2 Shrink-Wrap

Shrink-wrap is an alternative to stretch-wrap for unitisation. When shrink-wrap is exposed to a source of heat, the previously aligned (oriented) molecules try to return to the lower-energy, unoriented, random-coil conformation. The product prevents the film from returning to its unstretched dimensions, and the force exerted by the material on the product acts to unitise the load.

For unitising pallet-loads of goods, stretch-wrap is much more common than shrink-wrap, since it generally requires less energy and is more economical. Shrink-wrap is

more commonly used as a bundling wrap, unitising two or several products (either the same or different), rather than for full pallet-loads of goods.

Often, shrink-wrap is used for product protection rather than unitisation, in applications ranging from meat to toys. It can be designed to form a tight enclosure around the entire product, providing excellent protection against dirt, moisture and abrasion. Usually, the wrap is formed into a loose pouch before it is shrunk tightly around the product in a shrink tunnel, where the packaged product is exposed to hot air. LDPE and LLDPE are common materials for shrink films. PVC and PP are used in lesser quantities, as are some specialty films.

9.3.2 Bags, Sacks and Pouches

To make a bag, sack or pouch, two or more edges of a plastic film are sealed together, forming a cavity in which the product can be placed. In most applications, the opening is then closed so that the product is completely enclosed by the package. In some cases, such as merchandise sacks, one side remains open.

The terms 'bag', 'sack' and 'pouch' can be confusing. According to some authorities, sacks are larger than bags, and both refer to packages in which the top is open, while pouches are smaller, and refer to packages that are totally sealed. However, these definitions do not conform to common use of these terms, which, in practice, are often used interchangeably.

Common styles of pouches include pillow pouches, three-side-seal pouches and four-side-seal pouches. Pillow pouches are produced by forming the plastic film into a cylinder and sealing the edges together in what will become the back seam in the finished package. The bottom of the cylinder is collapsed and sealed, the product introduced, and then the top seam added. The shape of the filled package resembles a pillow – hence its name.

Three-side-seal pouches are formed, as the name indicates, by folding the film into a rectangle and sealing the three non-fold sides. In some cases, the fourth side is sealed as well, for additional strength. Four-side-seal pouches are formed from two pieces of material that are sealed together on all sides. Therefore, four-side-seal pouches need not be rectangular in shape. In contrast to pillow and three-side-seal pouches, the front and back of a four-side-seal pouch may be made from different types of plastic film.

In any of these pouch styles, gussets may be added to expand the capacity of the pouch without increasing its width or height.

Pouches may be used alone, or may be combined with another package for product distribution and/or sale. One very common package structure is bag-in-box packages, which consist of a pouch inside a folding carton or corrugated box.

The pouch material may be plastic film alone, or a multilayer material containing paper and/or aluminium foil. Paper may be used to add strength, rigidity, printability or bulk to the flexible package. Foil may be incorporated to improve the barrier to permeants such as oxygen, water vapour, odours or flavours.

In the past several years, stand-up pouches have increasingly been used as substitutes for cartons or bottles. Stand-up pouches are designed to stand upright on the retail shelf. Their design involves gussets and special shaping of the bottom panel.

9.3.3 Pouch Production

There are two primary ways of using bags, sacks and pouches for packaging: as preformed pouches, or in form-fill-seal operations. In a form-fill-seal (FFS) operation, the web stock (usually preprinted, if applicable) is fed into either a horizontal or vertical FFS machine, in which it is formed into a pouch, the product added and the final seal formed. If preformed pouches are used, the packages are formed and an opening left for product introduction. The product is added to the package in a separate operation, and then the package is sealed.

Form-fill-seal operations are usually economically advantageous for large-scale production. Buying of preformed pouches is generally more economical if production quantities are small, or in cases where the material is difficult to seal and poses quality control problems.

9.3.4 Dispensing and Reclosure Features

One of the long-standing drawbacks of flexible packaging has been the difficulty of providing easy-to-use and effective dispensing and reclosure. In the past few years, several innovations have provided significant improvements in these package attributes.

The most common way to dispense products from flexible packages is to cut or tear the package open, or to peel open one of the seams. For some products, such as breakfast cereal in bag-in-box packages, this is a significant source of consumer complaints. The seals often do not peel easily, and all too often the result is a bag with a split down the side, spilling cereal into the carton and making it nearly impossible to reclose the pouch to protect product freshness. Some flexible packages now incorporate zipper closures, often accompanied by a tear strip for initial opening. Other packages have resealable flaps, usually located along a seam.

For liquid products, some packages incorporate a threaded spout with a standard threaded cap. This may be located on the top of the pouch, or on the bottom, depending on the

product and the package size. In bag-in-box packages, the outer carton may include a flap through which the spout can be extended for dispensing. For single-serve drinks, it is common to provide an attached straw (protected from dirt in its own pouch, which is glued to the side of the drink pouch), along with a designated spot on the package that has been modified for easy puncturing.

9.4 Heat-Sealing

Heat-sealing is the usual method for producing seals and seams in flexible packaging. Occasionally, adhesive systems are used. There are a wide variety of types of heat-sealing systems, but the most common, especially for films, are thermal or bar sealing, and impulse sealing.

Thermal or bar sealing uses two heated bars that exert pressure on the materials to be sealed and at the same time conduct heat to the interface, melting the materials. The pressure ensures good contact between the materials, and assists in interpenetration of the melted viscous materials at the interface. When sufficient time has elapsed to produce an initial seal, the materials are released. Therefore, the hot tack of the material is crucial in forming an adequate seal. The full strength of the seal forms as the material cools, but the initial strength must be sufficient to maintain the seal integrity while cooling proceeds.

The sealing bars usually have rounded edges to avoid puncturing the material, and often one bar is fitted with a resilient surface to aid in achieving uniform pressure during sealing. Usually, the heat-seal jaws are serrated rather than flat, and produce a patterned seal. In variants of thermal sealing, only one bar is heated and the other is not. Especially for sealing lidding on containers, the bars may be shaped rather than rectangular, producing shaped seals. Another variant uses heated rollers rather than bars; the pouch is sealed as it travels through the rollers.

Impulse sealing also uses two jaws to produce the seal, but heat is generated by flow of an impulse of electric current through a nichrome wire. The jaws do not remain hot, but cool down after each electrical impulse. The material being sealed is captured between the jaws, the current flows to produce heating, and the material remains between the jaws for a cool-down period before it is released. Cooling may be aided by circulation of cooling water through the jaws. With impulse sealing, materials do not require as good hot tack as with thermal sealing. The seal will increase in strength during the cooling phase, before it is released from the heat-sealer, so it is not as subject to immediate failure or distortion. On the other hand, the impulse seal is typically much narrower than the bar seal, and therefore is often not as strong. Impulse sealing is particularly advantageous for oriented materials, which have a tendency to wrinkle during sealing. As with bar sealing, the jaws can be shaped to produce shaped seals.

Hot wire or knife sealing uses a heated wire or knife to cut and seal films simultaneously. It is often used to produce thin polyethylene bags for applications such as produce packaging. The seals are very narrow, often nearly invisible, and relatively weak. In band sealing, often used for the final seal on filled preformed pouches, the materials to be sealed are moved through heated bands. Both heating and cooling phases can be provided. Other types of heat-sealing are used less frequently in production of flexible packaging.

9.5 Other Uses of Packaging Films

Plastics films are sometimes used as components in rigid or semi-rigid packaging structures. They can serve as liners inside closures for bottles and jars, as lidding on trays or cups, or can be laminated on paperboard or other materials. While the plastic resins used as coatings are not produced as stand-alone films, they are deposited on or in packages as films. Two common packaging applications of plastic films outside the flexible packaging category are skin packaging and bubble-wrap.

In skin packaging, a product is held tightly to a backing material by a plastic film. Usually, the backing material consists of a heat-seal coated paperboard. The product is placed on the board, and then the heated plastic film lowered on to it. A vacuum is drawn through the backing material, causing the film to form tightly around the product and seal to the board. Usually, the product is displayed in the retail environment by hanging the backing from a peg. Obviously, the product must be able to withstand momentary contact with the hot plastic without damage, and the plastic must not adhere to the product. The coated backing often requires perforations to permit adequate evacuation of trapped air. In some cases, films are used that permit sealing to uncoated board. Heavy-duty films sealed to corrugated board can be used to provide protection to products during distribution, by physically isolating the skin-packaged product from impacts to the outer container.

Bubble-wrap is a cushioning material produced by forming bubbles of air, of a defined size, between two plastic films. The bubbles can be various sizes, depending on the end-use of the material. Generally, smaller bubbles are used to protect lighter-weight products, and larger bubbles are used for heavier products. Bubble-wrap does not provide suitable protection for products that are very heavy, however.

9.6 Major Packaging Films

A variety of plastic resins are used to make packaging films. Sometimes they are used alone, and often they are used in combinations that provide the benefits of multiple materials. The most commonly used packaging resins will be described in this section.

Table 9.1 Typical properties of polyethylene films [1, 2]			
Property	Polymer		
	LDPE	LLDPE	HDPE
Glass transition temperature (T_g ; °C)	-120	-120	-120
Melting temperature (T_m ; °C)	105-115	122-124	128-138
Heat distortion temperature, at 455 kPa (°C)	40-44		62-91
Density (g/cm ³)	0.915-0.940	0.915-0.935	0.94-0.97
Tensile modulus (GPa)	0.2-0.5		0.6-1.1
Tensile strength (MPa)	8-31	20-45	17-45
Elongation (%)	100-965	350-850	10-1200
WVTR* at 37.8 °C and 90% RH (g µm/m ² d)	375-500		125
O ₂ permeability, at 25 °C (10 ³ cm ³ µm/m ² d atm)	160-210		40-73
*WVTR: Water vapour transmission rate (d = day, 24 h) RH: relative humidity			

9.6.1 Low-Density Polyethylene (LDPE) and Linear Low-Density Polyethylene (LLDPE)

Low-density and linear low-density polyethylene are the most commonly used packaging films. Low-density polyethylene is produced by a high-temperature, high-pressure process that results in considerable short- and long-chain branching of the molecules. Linear low-density polyethylene is produced at temperatures similar to those used for high-density polyethylene, resulting in linear molecules. The reduction of density comes about through the use of comonomers that put side groups on the main chain that act like branching in decreasing crystallinity. In traditional Ziegler-Natta catalyst polymerisations, these comonomers are butene, hexene or octene. Some of the new family of polyethylenes using metallocene catalysts incorporate higher alpha-olefins into the polymer structure, producing longer side groups, which act much like the long-chain branching in high-pressure LDPE.

LDPE and LLDPE are soft, flexible materials, with a hazy appearance. At equal density and thickness, LLDPE has higher impact strength, tensile strength, puncture resistance and elongation than LDPE. LLDPE based on octene generally has the highest strength, followed by hexene- and butene-based polymers, in that order. The cost per unit mass of the materials generally also follows the order octene > hexene > butene. LDPE has better heat-seal properties than LLDPE. It seals at lower temperatures, seals over a wider temperature range, and has better hot tack, all of which result, to a great extent, from its long-chain branching. Metallocene LLDPE containing higher alpha-olefins was designed, in part, to remedy this disadvantage of LLDPE. Another approach that has commonly been taken to producing the best mix of properties for a given application is to blend LLDPE and LDPE.

LDPE and LLDPE are good barriers to water vapour, but are poor barriers to oxygen, carbon dioxide and many odour and flavour compounds. They have good grease resistance, and are quite inert. Low-temperature performance is good, as these materials retain their flexibility at very low temperatures. They soften and melt at moderately elevated temperatures, so they are not suitable for applications involving significant exposure to heat.

Some characteristic LDPE and LLDPE properties are presented in Table 9.1. LDPE is generally the cheapest plastic film, on a per-unit-mass basis. Since LLDPE often permits considerable down-gauging, it can be the lowest cost alternative on a per-use basis.

Very low-density polyethylene (VLDPE) is LLDPE with a higher concentration of comonomer, which reduces crystallinity, and consequently density, below the traditional range for LLDPE, to 0.905-0.915 g/cm³. These materials are very soft films, with excellent cling but reduced strength.

9.6.2 High-Density Polyethylene (HDPE)

High-density polyethylene is a linear addition polymer of ethylene, produced at temperatures and pressures similar to those used for LLDPE, and with only very slight branching. HDPE films are stiffer than LDPE films, though still flexible, and have poorer transparency. Their water vapour barrier is better, as is their gas barrier. However, permeability to oxygen and carbon dioxide is still much too high for HDPE to be suitable as a barrier for these permeants.

As is the case for LDPE, HDPE is very inert, and has good oil and grease resistance. Using high molecular weight (high molar mass) resin, HMW-HDPE, which permits considerable down-gauging, can reduce the cost of HDPE films on a per-use basis. This material is higher in cost per unit mass, and is also somewhat more difficult to process than lower molecular weight materials, due to its high viscosity. Another alternative for reducing the cost of HDPE film is the use of recycled material, often originating in milk cartons.

Because of the distinctly cloudy appearance of HDPE film, a small amount of white pigment is commonly added to provide an attractive opaque white film. Typical HDPE properties are shown in Table 9.1.

9.6.3 Polypropylene (PP)

Polypropylene is a linear addition polymer of propylene; resins used in packaging are predominantly isotactic. PP has the lowest density of the commodity plastics, 0.89-0.91 g/cm³. PP films are suitable for high-speed packaging applications that demand a relatively stiff material, since they are considerably stiffer than HDPE, and also have much improved clarity. Clarity can be further improved by using copolymer resins containing some ethylene units, to reduce crystallinity. Another approach to improving transparency is the use of nucleating agents to reduce average crystallite size. Barrier properties of PP are comparable to those of HDPE.

Unoriented PP film tends to be somewhat brittle, especially at low temperatures. In many applications, biaxially oriented film (BOPP) is preferred. Orientation also increases the stiffness of the film. PP, especially BOPP, does not heat-seal well. Therefore, it is commonly coated or coextruded with sealants to make heat-sealable films. Typical PP properties are shown in Table 9.2.

Property	Polymer		
	PP	BOPP	PVC
T _g (°C)	-10	-10	75-105
T _m (°C)	160-175	160-175	212
Heat distortion temperature, at 455 kPa (°C)	107-121		57-82
Density (g/cm ³)	0.89-0.91	0.89-0.91	1.35-1.41
Tensile modulus (GPa)	1.1-1.5	1.7-2.4	to 4.1
Tensile strength (MPa)	31-43	120-240	10-55
Elongation (%)	500-650	30-150	14-450
WVTR, at 37.8 °C and 90% RH (g μm/m ² d)	100-300	100-125	750-15,700
O ₂ permeability, at 25 °C (10 ³ cm ³ μm/m ² d atm)	50-94	37-58	3.7-240

9.6.4 Polyvinyl Chloride (PVC)

Polyvinyl chloride films are formed by combining PVC resin, produced by addition polymerisation of vinyl chloride, with plasticisers and other additives to produce a flexible film. Unmodified PVC is quite brittle and difficult to process because of its heat sensitivity. However, because of its polar nature, PVC has a high affinity for plasticisers, and hence can be substantially modified. Plasticisers generally consist of high-boiling-point organic liquids, which serve a lubricating function in the resin. Some soft and flexible PVC films are approximately 50% plasticiser by weight.

For food packaging uses, plasticisers and other ingredients must be suitable for direct food contact. The major plasticisers used in such applications are adipates. Often, epoxidised soybean oil is added as a secondary plasticiser. For non-food use, a wider range of plasticisers is available. Adipates and phthalates are most common. In addition to plasticisers, PVC films contain stabilisers, as the resin is heat-sensitive. Oil epoxides have some stabilising functionality, and in food packaging uses supplement the activity of calcium, magnesium or zinc stearates. Phosphites may also be used. In non-food applications, organometallic salts of barium and zinc are commonly used.

The properties of PVC films are strongly influenced by the type and level of modifying ingredients, especially plasticisers, that have been added. In general, the films are quite soft and flexible, easy to heat-seal, and have excellent self-cling, toughness, resilience and clarity. Permeability is relatively high. Both oriented and unoriented films are available. Properties of PVC film are listed in Table 9.2.

Heavier gauge PVC, sheet rather than film, is often used in thermoformed packaging, such as in blister packaging.

9.6.5 Polyethylene Terephthalate (PET)

Polyethylene terephthalate is formed by condensation polymerisation of ethylene glycol and either terephthalic acid or dimethyl terephthalate. It is commonly used in biaxially oriented form, and has excellent transparency and mechanical properties. Heat-setting enables the film to be used for extended periods at temperatures ranging from -70 to +150 °C. It can tolerate considerably higher temperatures for short periods, such as in dual ovenable packaging for frozen foods. PET has good barrier properties, especially for odours and flavours. The barrier properties can be enhanced by coating with PVDC, or by metallising, as will be discussed in subsequent sections. Coating or coextrusion is often used to provide good heat-seal properties. Typical PET properties are listed in Table 9.3.

Table 9.4 Typical properties of polyvinylidene chloride (PVDC) films [1, 2, 6]			
Property		PVDC polymer	
		General-purpose	High-barrier
T _g (°C)		-15 to +2	-15 to +2
T _m (°C)		160-172	160-172
Heat distortion temperature, at 455 kPa (°C)			
Density (g/cm ³)		1.60-1.71	1.73
Tensile modulus (GPa)		0.3-0.7	0.9-1.1
Tensile strength (MPa)		48-100	83-148
Elongation (%)		40-100	50-100
WVTR, at 37.8 °C and 90% RH (g µm/m ² d)		79	20
O ₂ permeability, at 25 °C (10 ³ cm ³ µm/m ² d atm)		0.31-0.43	0.031

Nearly all cellophane produced in North America is solvent-coated with PVDC copolymers. Solvent and latex coatings are also used on plastic sheet for thermoformed containers, and on blow-moulded plastic bottles. Common substrates include polyolefins, polyesters, polyamides and styrenics. Coextrusions of PVDC copolymer with polyethylene or polypropylene are used in shrinkable films for meat, cheese and other moisture- or oxygen-sensitive foods. Latex coatings of PVDC copolymers are used to provide moisture resistance, grease resistance and barrier to paper and paperboard packages.

9.6.7 Polychlorotrifluoroethylene (PCTFE)

Polychlorotrifluoroethylene (PCTFE) is another polymer with good barrier characteristics, especially for water vapour. The homopolymer is very difficult to process because of its extremely high melt viscosity. A small amount of modification by copolymerisation yields AlliedSignal Corporation's trademarked Aclar films, which contain greater than 95% chlorotrifluoroethylene by weight. These films are considered the best available transparent moisture barriers for flexible packaging; however, they are rather expensive.

Aclar films can be used alone, or can be laminated to paper, polyethylene, aluminium foil or other substrates. The film is heat-sealable, and can be thermoformed. Aclar blister packages are often used for unit packages for highly moisture-sensitive pharmaceuticals.

Table 9.3 Typical properties of polyethylene terephthalate (PET) films [1, 2, 5]			
Property		PET polymer	
		Unoriented	Oriented
T _g (°C)		73-80	73-80
T _m (°C)		245-265	245-265
Heat distortion temperature, at 455 kPa (°C)		38-129	
Density (g/cm ³)		1.29-1.40	1.40
Tensile modulus (GPa)		2.8-4.1	
Tensile strength (MPa)		48-72	220-270
Elongation (%)		30-3,000	70-110
WVTR, at 37.8 °C and 90% RH (g µm/m ² d)		390-510	440
O ₂ permeability, at 25 °C (10 ³ cm ³ µm/m ² d atm)		1.2-2.4	1.1

9.6.6 Polyvinylidene Chloride (PVDC)

Polyvinylidene chloride is an addition polymer of vinylidene chloride. It is an excellent barrier to oxygen, water vapour, odours and flavours. However, its high crystallinity and sensitivity to heat-induced degradation make it extremely difficult to process. Therefore, homopolymer PVDC is not used commercially.

Copolymerisation of vinylidene chloride with various amounts and types of comonomers, usually vinyl chloride, acrylonitrile, methacrylonitrile, methacrylates or alkyl acrylates, produces a family of PVDC copolymer resins with improved processability, while maintaining desired barrier properties. Vinylidene chloride content typically ranges from 72 to 94 wt%; molecular weights range from about 65,000 to 150,000 [6]. In general, the highest barrier resins are not melt-processable, but instead are applied by solvent or latex coating. Extrudable resins have undergone more modification, so consequently have somewhat decreased barrier properties. PVDC films produced for household use are plasticised copolymers, and have even poorer barrier performance. However, they remain much better barriers than competitive polyethylene films. Representative properties are shown in Table 9.4.

PVDC copolymer films can be heat-sealed. Therefore, in PVDC copolymer coatings or coextrusions, the PVDC can serve as a combination barrier and heat-seal layer. However, the best barrier films generally do not provide the best heat-seal capability, and vice versa, so when both heat-sealability and barrier are desired, sometimes two differently formulated PVDC copolymer coatings are applied.

Table 9.5 Typical properties of ethylene-vinyl alcohol (EVOH) films [1, 2, 7]		
Property	EVOH polymer	
	32 mol% ethylene	44 mol% ethylene
T _g (°C)	69	55
T _m (°C)	181	164
Heat distortion temperature, at 455 kPa (°C)		
Density (g/cm ³)	1.19	1.14
Tensile modulus (GPa)	2.6	2.1
Tensile strength (MPa)	77	59
Elongation (%)	230	380
WVTR, at 40 °C and 90% RH (g µm/m ² d)	1535	724
O ₂ permeability, at 25 °C (10 ³ cm ³ µm/m ² d atm)	0.0078	0.030

polyolefin, protects it. Monolayer EVOH films, oriented or unoriented, are also available, which can be used alone but are usually combined with other materials by laminating, or coating. Typical EVOH properties are listed in Table 9.5.

9.6.10 Polyamide (Nylon)

Polyamides, or Nylons, are a family of plastics containing characteristic amide functionality. They are commonly formed by condensation polymerisation of amino acids, or of carboxylic acids and amines.

Nylon films are used for specialty applications in packaging, where performance requirements justify their relatively high cost. Nylons have excellent high-temperature performance, so can be used, for example, in boil-in-bag packages. Nylons also provide excellent odour and flavour barrier, and reasonably good oxygen barrier. They are very poor water vapour barriers, and generally have a tendency to lose some barrier performance when exposed to large amounts of moisture. However, their performance is not as water-sensitive as EVOH.

Most Nylons used in packaging have some crystallinity; the amount is heavily dependent on processing conditions, since Nylons have a narrow window for crystallisation. Films generally retain good flexibility at low temperatures, and have excellent strength properties. Owing to their relatively high cost, they are often coextruded with other plastics.

9.6.8 Polyvinyl Alcohol (PVOH)

Polyvinyl alcohol films are unique in several respects. Polyvinyl alcohol polymers are produced by hydrolysis (more correctly, alcoholysis) of polyvinyl acetate. If fully hydrolysed, the polymer is readily soluble in water. Controlling the degree of hydrolysis can produce films that are soluble in hot water but not in cold water. Because PVOH degrades at temperatures well below melt, it cannot be processed by extrusion. Therefore, casting from a water solution is used to make film. As produced, the film is amorphous, but orientation induces some crystallinity.

The water-solubility of PVOH is the major reason for its use in niche markets where this is a desired attribute. One application is as an inner pouch in packaging of agricultural or other chemicals, to limit human exposure. The pouch with its contents can be placed into the dilution and dispensing apparatus, without direct contact between the user and the chemical. In the water, the pouch dissolves, releasing the chemical. The dissolved polymer does not clog spray nozzles, and is biodegradable.

Another application is in hospital laundry bags. Here, the hot-water-soluble variety is used. Soiled laundry is placed in the bags, and then bag and all can be placed into the washer, so that no contact between the launderer and the potentially infectious linen is required. Since the polymer does not dissolve in cold water, it will not be affected by residual liquid in the linens, but will dissolve readily in the hot wash water.

9.6.9 Ethylene-Vinyl Alcohol (EVOH)

Ethylene-vinyl alcohol resins are produced by hydrolysis (alcoholysis) of ethylene-vinyl acetate random copolymer, analogous to the route for production of polyvinyl alcohol from polyvinyl acetate. Commercially available materials contain a substantial percentage of ethylene, typically 27 to 48 mol%. The presence of ethylene renders the resins melt-processable.

The presence of -OH groups in the structure results in strong intermolecular hydrogen bonding. While EVOH is a random copolymer, CH₂ and CHOH groups are isomorphous; they fit into the same crystalline structure. Therefore, the polymer crystallises readily. The combination of strong intermolecular forces and crystallinity makes it an excellent barrier to gases, odours and flavours. However, the hydrogen bonds also make it a moisture-sensitive material, and high humidity decreases its barrier capability.

EVOH is most often used as an oxygen barrier. Since, in most applications, it is likely to be exposed to moisture either from the environment or in the product, it is usually used as a buried inner layer in a coextruded structure, where a good moisture barrier, often a

Table 9.6 Typical properties of polyamide (Nylon) films [1, 2]

Property	Polymer		
	Nylon-6	Nylon-11	Nylon MXD-6
T _g (°C)	60		64
T _m (°C)	210-220	180-190	243
Heat distortion temperature, at 455 kPa (°C)			
Density (g/cm ³)	1.13-1.16	1.03-1.05	1.20-1.25
Tensile modulus (GPa)	0.69-1.7	1.3	3.8-4.1
Tensile strength (MPa)	41-165	55-65	220-230
Elongation (%)	300	300-400	72-76
WVTR, at 40 °C and 90% RH (g μm/m ² d)	3,900-4,300	1,000-2,000	630
O ₂ permeability, at 25 °C (10 ³ cm ³ μm/m ² d atm)	0.47-1.02	12.5	0.06-0.26
Nylon MXD-6: Mitsubishi Gas Chemicals America, Inc., New York, NY, USA			

Polyamides manufactured from straight-chain amines and carboxylic acids are typically named with numbers representing the number of carbons in each of the starting monomers. For example, Nylon-6,10 is made from a six-carbon amine and a ten-carbon carboxylic acid. Similarly, polyamides made from amino acids have a number designating the number of carbons in the acid. When the carbons are not in a straight chain, more complex names are necessary. Typical properties of some Nylon films are given in Table 9.6. Nylon-6 tends to be the most-used Nylon packaging film in the USA, and Nylon-11 in Europe.

9.6.11 Ethylene-Vinyl Acetate (EVA) and Acid Copolymer Films

Ethylene-vinyl acetate is produced by addition copolymerisation of ethylene and vinyl acetate. The acetate groups provide polar functionality that increases intermolecular forces in the film, and, because of the structural irregularity thus introduced, interfere with crystallisation. These films have excellent transparency, and provide very good heat-seal and adhesive properties, with excellent toughness at low temperatures. Typical film-grade EVA resins contain between 5 and 18% vinyl acetate. Resins designed for use as an adhesive layer in a multilayer structure are typically at the higher end, and stand-alone films at the lower end, of this concentration range.

Common markets for EVA are poultry and meat wrap, stretch film and ice bags. The films tend to be sticky, so may require the use of slip and antiblock additives.

Copolymers of ethylene with acrylic acid and with methacrylic acid are also available, and are commonly called acid copolymer resins. They are characterised by good clarity, strong adhesion to polar substances such as paper, and also to foil, and low melt and heat-seal temperatures.

9.6.12 Ionomers

Ionomers are formed by neutralisation of ethylene-acrylic acid or ethylene-methacrylic acid copolymers containing 7 to 30 wt% acid, to yield sodium or zinc salts. The resulting ionic bonds function as reversible crosslinks in the polymer, readily disrupted by heat, but reforming on cooling. Therefore, these materials provide very strong bonding to numerous substrates. Ionomers can be used for skin packaging to uncoated corrugated board, for example.

The heat-seal performance of ionomers is outstanding, even permitting sealing through grease contamination, which makes them ideal for packaging of processed meat. They have superior hot tack, and excellent melt strength.

Ionomer films have excellent clarity, flexibility, strength and toughness. They can be used to package sharp objects, which break through many alternative materials when subject to vibration during distribution. Ionomers have relatively poor gas barrier, and tend to absorb water readily. They also are relatively high cost compared to films such as ethylene-vinyl acetate.

9.6.13 Other Plastics

Several other types of plastics are used in packaging films to some extent. Polycarbonate films have excellent transparency, toughness and heat resistance, but high cost. They have some use in skin packaging, food packaging where exposure to high temperatures for in-bag preparation is required, and medical packaging.

Polystyrene is another film with excellent transparency, often used in window envelopes and window cartons. It has low gas barrier, so can be used for produce where a 'breathable' film is required. In heavier gauges, polystyrene is widely used for transparent thermoformed trays. Expanded polystyrene is used for trays, egg cartons and other applications where its cushioning properties are desired. In general, these materials are

classified as sheet, rather than film. Polystyrene film is generally biaxially oriented to improve its properties, since the unmodified material is too brittle for most applications. Impact-modified polystyrene sheet that incorporates polybutadiene is often used where transparency can be sacrificed for impact resistance.

Cellulose-based plastics such as cellulose acetate, cellulose butyrate, cellulose propionate and copolymers are also used to a relatively small extent, most often as sheet rather than film. Their high price and water sensitivity limits their usefulness.

A wide variety of copolymers are available. Some of these have been discussed already. It is quite common to modify the chemical structure of a polymer to obtain a more desirable mix of properties. Another way to combine properties is to use blends of polymers. High-impact polystyrene (HIPS) is actually partially a copolymer and partially a blend of polybutadiene and polystyrene.

9.7 Multilayer Plastic Films

In many cases, the best combination of packaging attributes at the lowest cost is achieved by using a combination of materials. Therefore, plastic packaging films are often combined with one another or with other materials such as paper, aluminium or even glass, through processes such as coating, lamination, coextrusion and metallisation.

9.7.1 Coating

Coating is commonly used to add a thin layer of a plastic on the surface of another plastic film or sheet, or, more commonly, on a non-plastic substrate such as paper, cellophane or foil. The coating may be applied as a solution, a suspension, or a melt.

Common reasons for using coating in flexible packaging are: to impart heat-sealability for paper, cellophane, foil or plastics that are not themselves easily heat-sealed; to provide moisture protection for paper or cellophane; to improve barrier properties; and to provide protection from direct contact of the base material with the product.

Coating with low-density polyethylene is often used on paper to give heat-sealability and moisture protection, as well as to protect printing from abrasion. It is often used on aluminium foil to provide heat-sealability and abrasion resistance, and to prevent interaction between the foil and the product. PVDC copolymer coatings are often used to improve barrier and heat-sealability.

9.7.2 Lamination

Lamination is the process of combining two webs of film together. In flexible packaging applications, lamination is often used to combine a plastic film with paper or foil, or to join paper and foil together. A variety of lamination methods are used. When plastic films are involved, either as a substrate or as an element in the finished structure, the laminating adhesive is often low-density polyethylene, applied by extrusion, and the process is known as extrusion laminating. When paper is contained in a flexible package, it is most often being used for its excellent printability, along with its ability to impart substance and strength. When aluminium is used, it is most often employed for its excellent barrier to light and to permeation. Occasionally, it is used primarily for its desirable appearance.

Another significant use of lamination is to produce a web with buried printing. In these materials, one web is reverse-printed, and is then laminated to a second web, either made from the same or a different polymer. The printing can be seen through the transparent plastic, and is protected against abrasion so it maintains a fresh attractive appearance much better than surface-printed materials.

9.7.3 Coextrusion

Coextrusion results in the production of a multilayer web without requiring initial production of individual webs and a separate combining step. The melted polymers are fed together carefully to produce a layered melt, which is then processed in conventional ways to produce a plastic film or sheet. When only plastics are being used in a flexible packaging structure, coextrusion is generally preferred to lamination, unless buried printing is involved. Obviously, coextrusion cannot be used to incorporate non-thermoplastic materials.

A major advantage of coextrusion over lamination is its ability to incorporate very thin layers of a material, much thinner than those which can be produced as a single web. This is particularly important for expensive substrates, such as those often used to impart barrier properties. The amount of the expensive barrier resin used need only be enough to provide the desired performance. The thickness of the layer is not limited by the need to produce an unsupported film and handle it in a subsequent lamination step.

9.7.4 Metallisation

Metallisation is a way of applying a thin metal layer on a plastic film (or on paper), as an alternative to using a lamination with aluminium foil. In commercial packaging practice, the metal being deposited is almost always aluminium. The process, known as vacuum

metallising, involves evaporation of aluminium inside a vacuum chamber, and deposition of the aluminium vapour on a plastic film. The operation is usually done in a batch mode, with the substrate being metallised and an aluminium wire placed inside the vacuum chamber. The film is rolled past a chill roll, which removes the heat from the condensing aluminium, preventing melting of the film. Very high vacuums are needed, which has retarded the development of continuous metallisation processes, although some are available. Vaporisation of the aluminium is most often achieved by resistance heating. Induction and electron-beam heating are used to a lesser extent.

Metallised films have significantly enhanced barrier characteristics, and are usually chosen for this reason. Cost of metallised film is generally less than that of foil-containing laminated materials. In snack packaging, for example, metallised film has almost totally replaced foil laminations.

The barrier performance of metallised film, as initially produced, is somewhat inferior to foil, and is dependent on the thickness of the deposited metal layer. However, stress during product distribution can lead to the development of flex cracks in foil, which then provide a route for gas transfer. Metallised foil, since it retains the flexibility and other mechanical characteristics of the film substrate, is not usually subject to flex cracking. Therefore, the barrier characteristics of metallised foil are sometimes superior to those of foil laminations, at later points in distribution. Also, many oxygen-sensitive products require better barrier than can be attained with plastic alone, but can be successfully protected with metallised film. In addition to gas barrier, metallised film provides an essentially total light barrier.

Occasionally, metallised foil is used for its appearance, rather than for its barrier characteristics. This is particularly the case when it is used for labels. In many such applications, however, paper, rather than film, is the metallisation substrate.

9.7.5 Silicon Oxide Coating

One of the disadvantages of metallised film is that the resultant material is opaque, and is not suitable for use in microwave ovens. The desire for transparent high-barrier coatings led to the development of glass-like coatings based on silicon oxide, SiO_2 .

Silicon oxide coatings on film are usually applied in a manner analogous to vacuum metallising. The silicon oxide is evaporated, using electron-beam heating, and condensed on the film substrate in a vacuum chamber. The film is very thin, 400 to 1000 Å, and does not affect the mechanical properties of the material to any significant degree. The chemical composition of the deposited film depends somewhat on conditions, and is

characterised as SiO_x , where the value of x is between 1.0 and 2.0. At values close to 1, the layer imparts a distinct yellowish colour to the film. At values close to 2, it is nearly colourless. The yellowing is a significant concern in some applications. The SiO_x layer greatly increases barrier of the film, and it is transparent to microwave radiation. Therefore, it can be used in packages that will be heated in microwave ovens. The most common substrate is PET, in thickness of 12.5–25 µm, although polypropylene, polystyrene and polyamides can also be used.

An alternative to evaporative deposition is chemical plasma deposition, in which a silicon-containing gas such as tetramethyldisiloxane or hexamethyldisiloxane is used as the silica source. Little heat is required, and the degree of vacuum needed is lower. Therefore, plasma deposition can be used on heat-sensitive materials such as LDPE and oriented PP. The coating produced is thinner, and less yellow. Plasma deposition is the method of choice for SiO_x coating of containers, and can also be used for film.

9.7.6 Other Inorganic Barrier Coatings

Processes have also been developed that deposit aluminium oxide coatings on plastic films, to increase barrier properties. Combinations of SiO and MgO have also been used.

Another type of inorganic barrier coating uses clay nanocomposites, which are deposited on the film from a solution of PVOH/EVOH copolymer, in a mix of water and isopropyl alcohol, with nanodispersed 7 nm diameter silica and titanium dioxide particles. Microgravure equipment is used to coat the solution on to the film substrate. Barrier is reportedly comparable to that of films metallised with aluminium, but the coatings are transparent.

These materials are all still in relatively early phases of development.

9.8 Surface Treatment

In many packaging applications, it is necessary for something to stick to a plastic film. This may involve placing a label on a pouch or on a stretch-wrapped pallet, adhering two films together in a lamination, or, as is often the case, printing the film. Adequate adhesion requires that secondary bonding forces between the film and the object, such as the ink, which is to be adhered, be sufficient to retain the material. Historically, this has been a significant problem for plastic films, since the surface energy of the films is often low, causing poor adhesion. Several techniques are commonly used to increase the surface energy of polymers, hence improving adhesion. For films, the most common treatment is corona discharge.

In corona discharge treatment, the film surface is exposed to a discharge between grounded and powered electrodes, at high voltage. The discharge of the electric current ionises the air in the gap between the electrodes. The ions produced initiate free-radical reactions with the film surface, causing bond cleavage followed by oxidation. Oxidation of the surface increases its ability to adhere to substances such as inks and adhesives. The effectiveness of corona discharge treatment dissipates with time, so ideally it should be applied within a short time of the subsequent printing. In a roll of corona discharge-treated material that has been stored, the effectiveness of the treatment is likely to be significantly higher on the inside layers than on the first few outside layers of film.

Other surface treatments that are sometimes applied to film also exist. However, corona discharge is by far the most frequently encountered.

9.9 Static Discharge

Plastics, because they are nonconductive, are subject to build-up of electrostatic charges. When such charges build up, the result can range from the attraction of dust and lint to material handling problems, shocks and sparks. Methods for controlling the build-up of static charges include charge neutralisation through ionisation of the surrounding air and incorporation of conductive materials to dissipate the charge.

Antistatic agents can be incorporated into the film as additives, or can be used as a surface treatment. The agents commonly used include non-ionic ethoxylated alkylamines, anionic aliphatic sulfonates and phosphates, and cationic quaternary ammonium compounds. In some cases, humidifying the area can control static, so that a thin layer of water is absorbed on the film surface, which conducts the charge to ground.

Control of static discharge is especially important for packaging for sensitive electronic devices. Film designed for such applications, usually polyethylene, is generally pigmented pink to denote that it contains antistatic agents.

9.10 Printing

In many packaging applications, plastic films are printed to convey information to the user. When printing is desired, it is usually done on roll stock before packages, such as pouches, are formed. Printing on formed flexible packages is usually limited to date or lot coding.

Flexography is the printing method used most often for flexible packaging materials. In this process, a subcategory of relief printing, the printing plates are flexible elastomers,

with the images, or printing areas, raised above the nonprinting surrounding areas. Thin, highly fluid, rapid-drying inks are used. The ink is transferred by a system of rollers to the top surface of the printing plates, which in turn transfer the ink to the film.

In lithography, the printing image and the background are on the same plane of the thin metal printing plate. The plate is treated to attract water and repel ink in the non-image areas, and the reverse in the image areas. A system of rollers is used to transfer both ink and water to the plate. The image on the plate is then transferred (offset) to a rubber-blanket-covered cylinder, and then to the film.

Rotogravure uses copper-plated printing cylinders, which have the image engraved into the cylinder in the form of tiny cells. The cylinder rotates in an ink bath, filling the cells with ink. Excess ink is wiped off by a doctor blade, and then the image is transferred to the film as it is pressed against the printing cylinder by an elastomer-covered impression cylinder.

For printing date and lot codes on formed packages, ink-jet printing is commonly used. In this process, electrically charged drops of ink are sprayed out of jets, and electrostatically directed to the desired printing location. This is an impactless form of printing, and is ideal for printing rapidly changing information such as these codes.

Other types of printing, such as screen printing, as well as variations of the basic processes described above, are used less frequently for plastic packaging films.

9.11 Barriers and Permeation

As has been discussed, in many packaging applications, protection of the product from gain or loss of gases or vapours is important. The mechanism by which substances travel through an intact plastic film is known as permeation. It involves dissolution of the penetrating substance, the permeant, in the plastic, followed by diffusion of the permeant through the film, and finally by evaporation of the permeant on the other side of the film, all driven by a partial pressure differential for the permeant between the two sides of the film.

The barrier performance of the film is generally expressed in terms of its permeability coefficient. For one-dimensional steady-state mass transfer, the permeability coefficient is related to the quantity of permeant, which is transferred through the film as represented by the equation:

$$\bar{P} = \frac{Ql}{At\Delta p} \quad (9.1)$$

where $\bar{P}$ is the permeability coefficient, Q is the mass of permeant passing through the material, l is the thickness of the plastic film, A is the surface area available for mass transfer, t is time, and Δp is the change in permeant partial pressure across the film.

It can be shown that the permeability coefficient, as defined by equation (9.1), is equal to the product of the Fick's law diffusion coefficient, D , and the Henry's law solubility coefficient, S , in situations where these laws adequately represent mass transfer (ideally dilute solutions, diffusion independent of concentration):

$$\bar{P} = DS \quad (9.2)$$

The permeability coefficient, under these circumstances, is a function of temperature, but is not a function of film thickness or permeant concentration.

While this is a very simplified approach to mass transfer, it is adequate for many packaging situations. For example, with oxygen-sensitive products, reaction with oxygen is commonly rapid compared to the rate of transfer, so the oxygen concentration within the package is relatively constant at nearly zero. Oxygen concentration in the surrounding air, measured as partial pressure, is constant at approximately 21 kPa. Regardless of the shape of the flexible package, mass transfer is essentially one-dimensional, through the thickness of the film. If temperature is constant and $\bar{P}$ is known, the amount of oxygen transported through the film in a given period can be easily calculated using equation (9.1). Conversely, if the sensitivity of the product is known in terms of the maximum amount of oxygen that can be taken up without resulting in unacceptable product quality, the time required for that amount of transfer (the product shelf-life) can be calculated.

A similar approach can often be taken for transfer of odour or flavour compounds. While the diffusivity, and hence the permeability coefficient, of such organic substances is likely to be concentration-dependent, at the low levels associated with most packaging situations, the dependence is slight.

Calculating shelf-life when water vapour transmission is involved is more problematic. In such cases, the partial pressure difference for water vapour between the inside and the outside of the package is almost never constant. Simplifying assumptions generally used consider the time for moisture in the product itself and in the product headspace to reach equilibrium to be small compared to the time required for permeation, and ignore moisture change in the headspace itself, calculating only moisture gain or loss in the product. The resulting differential equation is:

$$\frac{dQ}{dt} = \frac{1}{l} \bar{P} A (p_2 - p_1) \quad (9.3)$$

where p_1 is the partial pressure of water vapour outside the package, p_2 is the partial pressure of water vapour inside the package, and p_2 is a function of Q . Solution of this equation requires knowledge of the moisture sorption isotherm for the product, which relates the moisture content of the product to the equilibrium relative humidity of the air in contact with the product, and thus to p_2 .

In the case where the sorption isotherm at the storage temperature can be approximated as linear over the range of moisture contents of interest, it can be written as:

$$W = a + bM \quad (9.4)$$

where W is the water activity of the air in equilibrium with the product with moisture content M (dry weight basis), and a and b are the best-fitting straight-line constants. Rewriting the basic permeability equation [equation (9.3)] in terms of water activity, and substituting:

$$Q = (M - M_i)w \quad (9.5)$$

where M_i is the initial moisture content and w is the dry weight of the product gives:

$$w \frac{dM}{dt} = \frac{\bar{P} A p_s}{l} (W_2 - W_1) \quad (9.6)$$

where W_1 and W_2 are the water activities at times 1 and 2, and p_s is the saturation water vapour pressure at the storage temperature.

This equation can be integrated, giving the following relationship for moisture gain or loss:

$$-\frac{1}{b} \ln \left(\frac{W_2 - W_1}{W_2 - W_1|_0} \right) = \frac{\bar{P} A p_s t}{lw} \quad (9.7)$$

Mass transfer characteristics for plastics are often expressed in terms of water vapour transmission rates (WVTR), rather than permeability coefficients. WVTR reflect the rate of water vapour transfer under specific conditions, and must be translated to permeability coefficients for application at different conditions. The relationship between $\bar{P}_{\text{water}}$ and WVTR is the following:

$$\bar{P}_{\text{water}} = \frac{\text{WVTR}}{\Delta p} \quad (9.8)$$

where Δp is the difference in water vapour partial pressure under the conditions at which the WVTR was measured. In many cases, this was the ASTM standard condition of 32.2 °C (90 °F) and 90% relative humidity (RH).

When permeability coefficients are not available at the temperature of interest, an Arrhenius relationship can be used to determine the required value, from the permeability coefficient at a nearby temperature and the activation energy. The equation used is the following:

$$\bar{P}_2 = \bar{P}_1 \exp\left\{\left(\frac{E_a}{R}\right)\left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right\} \quad (9.9)$$

where T_1 is the temperature at which $\bar{P}_1$ is known, T_2 is the temperature at which $\bar{P}_2$ is to be calculated, E_a is the activation energy, and R is the gas constant.

Care must be taken in applying equation (9.9). The permeability coefficient, as indicated, is a product of the diffusion coefficient and the Henry's law solubility constant. Since these vary in different ways with temperature, equation (9.9) is valid only over reasonably small temperature ranges. A particular concern is that permeation rates are much higher above the T_g than below this temperature, and the rate of change with temperature differs. Therefore, equation (9.9) should never be used to calculate the permeability coefficient across a temperature range that spans T_g of the plastic.

Permeability coefficients for multilayer plastic film or sheet, either coextrusions or laminations, can be calculated from the thickness and permeability coefficients of the individual layers, as follows:

$$\bar{P}_t = \frac{l_t}{\sum_{i=1}^{i=n} (l_i / \bar{P}_i)} \quad (9.10)$$

where the subscript t indicates the value for the total structure, i indicates the value for an individual layer, and there are n layers in the structure.

Special care must be taken when the barrier characteristics of a polymer are affected by the presence of the permeant or of some other substance that may also be permeating. This situation is most often encountered with water-sensitive plastics, such as ethylene-vinyl alcohol, since co-permeation of water vapour and other components of interest, such as oxygen, may well occur during processing and storage. It may also arise in other situations, such as co-permeation of organics involved in odour and taste.

9.12 Environmental Issues

In recent years, consideration of the environmental effects of packaging decisions has become more common. While thorough discussion of such issues is beyond the scope of this chapter, some general observations and conclusions will be made.

It is generally agreed that evaluation of the environmental impacts of a product or package requires consideration of the total life-cycle of the object. Such 'cradle to grave' analysis is commonly referred to as life-cycle assessment. Usually, when such analyses are carried out, the most influential life-cycle stage is that of production of the raw materials and packages, rather than transportation or disposal. Packages that minimise material use are therefore likely to have reduced environmental impact. Since flexible packaging systems usually (although not always, since distribution packaging must be included) use less overall packaging material, they often have reduced environmental impact, compared to the rigid packaging systems they replace.

In examining the impacts of waste disposal, two general conclusions can be drawn. In most cases, flexible packaging is less likely to be recovered for recycling than rigid or semi-rigid packaging. Therefore, a higher proportion of flexible packaging is likely to require disposal. On the other hand, flexible packaging, as discussed above, usually means less total material requires handling. Unless recycling rates for the alternatives to the flexible packages are very high, use of flexible packaging is likely to mean less material requiring disposal. Also, flexible packages containing plastics are sources of recoverable energy in appropriate systems.

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10 Applications of Plastic Films in Agriculture

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10.1 Introduction

The quantity of plastic materials used annually in the world in the agricultural sector amounts to 2 million tons. About 50% of this is used in protected cultivation greenhouses, as mulching, for low tunnels, as temporary coverings of structures for fruit trees, etc. [1]. Thin plastic film produced with low investment is economically and technically feasible, and provides the best cost/benefit ratio for use in greenhouses and low tunnels. The area covered by both greenhouses and tunnels has been experiencing continual growth. This growth is expected to appear in many countries where protected cultivation replaces the traditionally used more expensive glass-clad greenhouses.

Low-density polyethylene (LDPE), ethylene-vinyl acetate (EVA) and linear low-density polyethylene (LLDPE) films are the most common greenhouse covering films in agriculture. This chapter looks at the production of polyethylene-based plastic films for protected cultivation. The mechanical properties that make these films suitable for the use in agriculture are discussed. The stability of these plastic films under the effects of different environmental conditions is reported. These include solar irradiation, temperature, humidity, wind, fog formation and pesticides. Types of ultraviolet (UV) stabilisers and a determination of their compatibility are given. Also, the recycling of plastic films used in agriculture is of great importance, and a case study of their recycling as agricultural films is given.

10.2 Production of Plastic Films

LDPE films dominate the market for protected cultivation in the countries of both the Mediterranean region and worldwide. Most of these contain special additives, which are used either to enhance the performance of the film in the special conditions met in a greenhouse, or to prolong its lifetime by minimising the effects of the environment on the structure of the film.

Advances in the formulation of the LDPE films in use today have led to an expected lifetime of between one and five cultivating seasons [2]. The expected lifetime is, in fact, significantly affected by the environmental conditions that the film will face during its use. The climate of the region, the greenhouse design, the microclimate developing inside

the greenhouse, the use of agrochemicals and the environmental pollution of the area can all severely affect the lifetime of the material by inducing ageing of the plastic film to various degrees. Thus, a film whose lifetime is estimated to be four seasons in North-Central Europe will only last two or three seasons in the Mediterranean [2].

The varying requirements for greenhouse systems between different regions because of different climatic conditions and differences in production methods has led, until very recently, to a significant variation in approaches, standards and practices adopted or implemented by the interested National Research Institutions, Commercial Agencies and relevant industries [3]. Some of the consequences of this differentiation and variability are reflected in the lack of standardisation concerning the testing methods for covering materials of greenhouses. Usually, the testing methods used for plastics in general are also applied to greenhouse covers, despite important functional differences. As a consequence, quality control data provided by the producers of the covering materials of greenhouses are usually limited to only a few properties of these materials. In most cases, it is not possible to reproduce the relevant technical information provided, as this is not obtained systematically and is available in a somewhat confusing way [3]. The manufacturing of plastic films used in agriculture is usually carried out by blown film extrusion (tubular extrusion). Readers are asked to consult Chapters 1 and 2, where the manufacturing process is given in detail.

10.3 Characteristics of Plastic Films Used in Agriculture

The film products of interest here have been evaluated for their applied efficiency on the basis of their characteristics and requirements related to mechanical resistance, total percentage light transmittance ($T\%$) to visible solar and long-wavelength ultraviolet (UV-A) radiation, useful lifetime and energy-saving potential (greenhouse effect). Visible solar radiation regulates the nutrition of plants through the 'chlorophyll function'. Long-wavelength ultraviolet radiation favours the formation of pigments and vitamins, which is advantageous for the quality characteristics of the crop involved, with regard to flavour, intensity of colour, perfume or smell and good keeping of fruit or vegetables.

With reference to energy saving, values of the total thermal transmittance measured in $W/m^2\ ^\circ C$ for the different covering materials and their possible combinations have been estimated. The total thermal transmittance of a covering material indicates the general heat loss (management, convection, radiation), estimated in watts, through a $1\ m^2$ surface referred to a difference of $1\ ^\circ C$ between the internal and external environmental temperatures of the prepared covering. These values enable estimation of the theoretical thermal yield of a manufactured film related to the heating needs for a thermal difference of $1\ ^\circ C$ across the film.

The incident heat calculation enables the agricultural operator to choose the proper covering material with respect to any thermal ($^\circ C$) and luminous (flux) needs of the species to be established in the agricultural crop rotation desired. This can be done by using the results showing the total thermal transmittance ($W/m^2\ ^\circ C$) and total light transmittance ($T\%$) of some materials for greenhouse covering [4].

10.4 Stability of Greenhouse Films to Solar Irradiation

The performance and lifetime of the plastic films used as covering materials in protected cultivation depend strongly on: (a) the original chemical structure of the materials, (b) the change in the properties of the material brought about by induced ageing, (c) the type of physical structure used, (d) the climatic conditions of the area where the structure is installed, and (e) the use of agrochemicals, among other things. A brief description of the factors affecting the stability of polyethylene (PE) as a greenhouse covering under the effect of different environmental conditions is given below.

It is well known that photodegradation of many plastic materials occurs on subjecting these materials to solar radiation with wavelengths of 290-1400 nm [5, 6], the most energetic part of the solar spectrum. UV radiation in the range 290-400 nm can be absorbed by the plastic, and this is followed by bond cleavage and depolymerisation, causing photodegradation.

The photodegradation process of the covering materials of a greenhouse is further complicated by various interacting factors. The effect of UV radiation combined with varying temperature, humidity, critical mechanical loads, friction, abrasion, exposure to agrochemicals, etc., accelerate ageing at various rates. Accordingly, it is difficult to predict the lifetime of plastic films by laboratory testing of the photostability of films. For instance, high abrasion of the film by sand or soil particles carried by the wind leads to the formation of high concentrations of active centres giving rise to an increase in photodegradation.

10.4.1 Ultraviolet Stabilisers

Theoretically, LDPE should be stable under the effect of UV due to its stable structure and the absence of chromophores. However, during processing, it suffers partial oxidation, in which carbonyl and hydroxyl groups are formed. Also, it contains some impurities (photo-absorbing chromophores). Both impart photosensitivity to LDPE films [7, 8].

Special measures are therefore needed in order to protect greenhouse films against solar radiation and especially its most energetic and therefore harmful portion, namely, UV

radiation. Inhibition or at least retardation of the reaction responsible for degradation is, of course, a necessity for successful UV stabilisation. Retardation or protection against photodegradation can take place by using additives. These additives may retard the photodegradation of the polymer in three ways, namely, ultraviolet screening, ultraviolet absorption and excited-state quenching. Thus, stabilisers are often included in the polymer to provide stability against photooxidation to protect the material from UV light damage. The effectiveness of a light stabiliser depends on many factors, including its solubility and concentration in the polymer matrix [9].

10.4.1.1 Ultraviolet Screening

Ultraviolet screening compounds are based on inorganic or organic additives. In this type of protection, the ultraviolet light is blocked before it can reach the polymer. Screening is provided by pigments or by reflective coatings. Carbon black is also very effective and is used to stabilise many outdoor grades of polymers. In this case of UV screeners, any damage is confined to surface regions because UV penetration is restricted to very short distances. However, many of the pigments, like chalk, talc, short glass fibres and carbon black, impart an unattractive appearance, the grey, brown and black colours generally being unappealing. TiO_2 is another common additive, which may act as a screener, but it may occur in different forms, some of which are chemically active and can promote photodegradation.

The first class of organic additives for improving the resistance to UV radiation is the UV absorbers. They act by absorbing the harmful UV radiation above 290 nm, and thus do not allow it to reach the chromophores present in the chemical structure of LDPE as a result of processing or as impurities.

Many organic compounds absorb light in the desired region but few act as stabilisers. Some have little or no effect when added to polymers and may actually increase the rate of degradation. For a UV absorber to be effective, it must be able to dispose of its excitation energy without interacting with the polymer in harmful ways and without undergoing any photochemical reaction that would destroy its effectiveness. Accordingly, a stabiliser must have a structure that provides a rapid cascade back to the ground state through thermally excited levels with a quantitative efficiency for return to the ground state not less than 0.999%, i.e., less than one molecule can be destroyed for every 100,000 molecules that are excited.

Derivatives of *o*-hydroxybenzophenone or benzotriazole are examples of UV absorbers. However, this class of stabilisers seems to perform better in thicker materials and not well in the thin LDPE greenhouse films [8].

10.4.1.2 Excited-State Quenchers

The second class of UV stabilisers is the nickel excited-state quenchers. These quenchers act by deactivating the excited states of the chromophoric groups responsible for the photo-initiation by energy transfer, instead of relying on direct absorption of the UV radiation [8]. With proper selection of the Ni quenchers, the results of the UV stabilisation are satisfactory. A typical example of a nickel excited-state quencher is nickel dibutyldithiocarbamate. However, formulations containing such Ni quenchers are prohibited because of the environmental impact of nickel compounds.

10.4.1.3 Hindered-Amine Light Stabilisers (HALS)

HALS, based on bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, are the most recent and innovative class of light stabilisers. HALS do not absorb any light above 250 nm and so cannot be regarded as UV absorbers or as excited-state quenchers. Through oxidation of the piperidyl group to the nitrosyl group, a radical becomes available that starts a very efficient cycle of radical scavenging and peroxide decomposition. Thus, HALS are converted to the corresponding nitroxyl radicals, which are the real species responsible for polymer stabilisation. Hindered nitroxyl radicals are effective chain breaking antioxidants that act by trapping alkyl radicals to give hydroxylamines and/or alkylhydroxylamines – the former regenerates nitroxyl. The overall high efficiency of HALS as UV stabilisers in polyolefins is attributed to the regeneration of the nitroxyl radical. The complementary nature of the chain breaking antioxidant mechanisms involved [10] are shown in Scheme 10.1. From these reactions, nitroxyl and alkoxy radicals are formed according to equations (10.1) and (10.3)-(10.5). These radicals act as scavengers for any radicals formed during UV irradiation [equation (10.2)].

This means that HALS operate as excellent antioxidants. Some of the HALS contain further antioxidant groups; others are polymeric and less extractable. The main difference between UV absorbers and HALS is that the former absorb UV radiation and in turn are destroyed by it, while the latter do not absorb UV radiation and are much more slowly altered by secondary side reactions.

Thus HALS act as radical traps for radicals produced from photochemical oxidation [8, 9]. They offer an excellent approach to ultraviolet stabilisation and have replaced nickel quenchers and ultraviolet absorbers in many applications. Highly efficient chemically resistant light stabiliser systems have been developed. Market demands for extended-life greenhouses and thinner mulch films require even more powerful stabilisers. New non-interacting chemistries based on alkoxylamine HALS will offer a new generation of stabilisers for agricultural polyethylene films.

Stabilisers are normally dissolved in the polymer melt at the processing temperature. However, their solubility limit may be exceeded on cooling and this may lead to visually observable blooming. These processes depend on the nature of the chosen substrate as well as on its morphology.

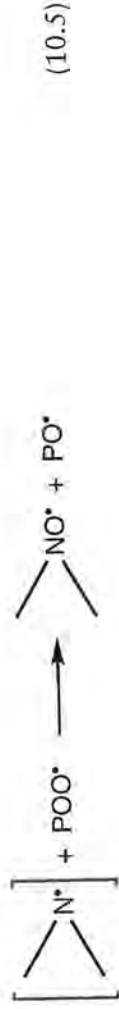
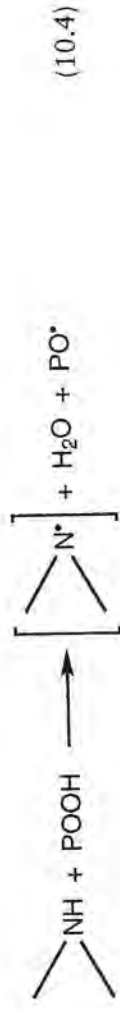
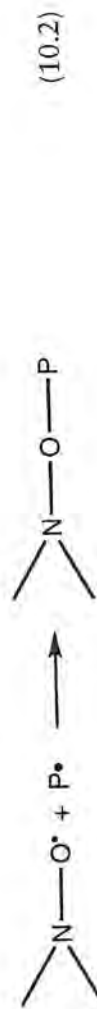
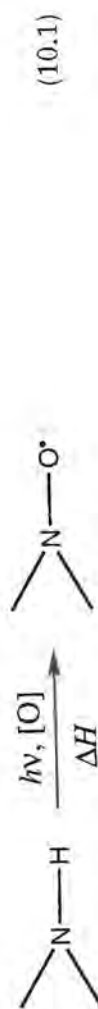
Additive diffusion is primarily a consequence of the thermal motion of the polymer chains above the glass transition temperature and of the related formation and disappearance of free volumes. If the chains are flexible and move easily, only small amounts of energy are necessary to move the polymer segments.

With increasing orientation of the polymer chains or on crosslinking and with increasing crystallinity, the diffusion constant decreases. For this reason, the diffusion of additives is faster in LDPE than in high-density polyethylene (HDPE). Numerous studies [11-14] confirm that the diffusion behaviour of UV absorbers depends mainly on polymer structure and morphology and to a minor extent on additive structure.

The solubility and compatibility of light stabilisers are particularly a problem when highly polar light stabilisers are used for non-polar plastics such as polyolefin. However, even in polyurethane, the compatibility of light stabilisers may become a problem.

10.4.2.2 Determination of Compatibility

Stabilisers such as antioxidants, metal deactivators and UV absorbers are added to polymers to reduce degradation during the manufacturing process and throughout the lifetime of the polymer products. In order to study the degradation of polymers or the compatibility between additives and polymers, it is essential to have an analytical method that can provide both identification and a quantitative measure of additives in the polymers. Fourier transform infrared (FTIR) spectroscopy [15, 16], UV spectroscopy [17], near-infrared reflectance gas chromatography, high-performance liquid chromatography (HPLC) and differential scanning calorimetry (DSC) can all be used as analytical tools for identification and determination of the concentration of dissolved stabilisers and their homogeneous distribution. FTIR and UV spectroscopy are the most important techniques used, as they can be applied directly to the sample without disturbing the morphology in the solid state. In addition, it is possible to detect any degradation or changes taking place at earlier stages due to the sensitivity of these tools. Furthermore, the diffusion coefficient of additives can be estimated by using the disc-stacking technique [18], where a disc doped with the additives is placed in the middle of a stack of undoped discs. Diffusion is then allowed to take place at an appropriate temperature for an appropriate time. Then spectroscopic measurements can be done on different discs to evaluate the concentration of the additives in each disc. Accordingly, the diffusion



Scheme 10.1

10.4.2 Requirements for Stabiliser Efficiency

The effectiveness of long-time stabilisation depends not only on the chemical nature but also on the rate of additive loss, which in turn depends on the compatibility of the additive with the polymer and is controlled by its volatility, solubility and diffusion coefficient.

10.4.2.1 Compatibility of the Additive

Compatibility is the main problem for light stabilisers, because light stabilisers are generally used in concentrations up to 2%. Ideally, stabiliser molecules should be disposed singly throughout the polymer matrix. This will not generally happen, but compatibility with the polymer should be sufficient to prevent gross phase separation.

polymer inter-chain distance. This equation was found to be valid not only for the relaxation process of an additive in a polymer but also for the δ relaxation process of side-chain liquid-crystalline polymers and their additives. This equation implies that, if the molecules are molecularly dispersed, and have a length not longer than 1.8 nm, they must relax cooperatively with the cooperatively reorienting segments of the glass process at the same relaxation frequency. However, in the case of Tinuvin P, a commercially available UV stabiliser (a benzotriazole derivative), the difference in the relaxation frequency maxima of the stabiliser peak and the glass process of the matrix, $\Delta \log f_m$, is greater than three decades of frequency. These results indicate that the reorientations of the stabiliser are not coupled with the glass process of polystyrene segments, where the stabiliser molecules can relax locally at higher frequencies, (i.e., faster by a factor of 1000). Furthermore, short additives can relax either cooperatively with the polymeric segments at the same relaxation frequency as the segments, or locally at higher frequencies. The ratio of the local contributions to the total relaxation strength (cooperative plus local) of the additives depends on the size of the stabiliser.

The biodegradation of representative samples of available commercial photo(bio)degradable polyethylene films was examined with respect to the rate and extent of degradation, oxidation products and changes in molecular weight both during outdoor exposure and in laboratory photo-ageing devices with different accelerating factors [23]. Although the rate of photooxidation was found to depend on the type of degradation system used, all the samples showed a rapid rate of carbonyl formation, with concomitant reduction in molecular weight and mechanical properties on exposure to UV light. The photo-fragmented polymers were shown to be much more hydrophilic in nature compared to the unoxidised analogues, and photo-fragments of all samples were found to contain high levels of low molecular weight (low molar mass) bioassimilable carboxylic acids and esters.

The recycling behaviour of virgin polyolefins, both as homopolymers and as heterogeneous polymer blends, which contained 10% of non-oxidised and photooxidised photo(bio)degradable plastics, has been examined. It was found that the initial mechanical performance of homogeneous blends was not greatly affected by the presence of non-oxidised degradable materials. However, blends containing degradable films that were initially partially photooxidised had a much more detrimental effect on the properties of the recycled blends during processing and weathering; the effect was minimal for degradable polymers containing the iron-nickel dithiocarbamate system.

10.4.3 Evaluation of Laboratory and Outdoor Photooxidation

Laboratory and outdoor photooxidation of plastic films were evaluated using different techniques [24]. Thus melt blown, biaxially oriented, unstabilised and stabilised LDPE films with various thicknesses were exposed in two accelerated artificial weathering devices

coefficient can be determined by knowing both the thickness of the discs and the concentration of the additive by using a characteristic absorption band.

The principle behind the use of near-infrared reflectance analysis is the measurement of the light reflected by a sample when exposed to light in this region. The logarithm of the inverse of this reflected light can be related to the concentration of a particular component found in the sample. The obtained concentration value for different discs can also be used for determination of either the diffusion coefficient or the solubility of the additive. The same can be said for gas chromatography or HPLC. On the other hand, differential scanning calorimetry can be used to determine the exothermic peak of the oxidation of antioxidants, which allows direct determination of the concentration of the dissolved antioxidants.

However, the commonly used methods for determination of compatibility do not give adequate information about the molecular association of the stabilisers, but only information about the volume concentration of the stabilisers in the polymeric matrix. This means that it makes no difference whether the stabilisers are present as stacks of molecules or as single molecules. Such aggregation will lead to lower efficiency of stabilisers. Of course, FTIR can offer some information from the change in the perturbation potential that results from polymer-stabiliser and stabiliser-stabiliser molecular interactions.

However, this needs a very careful study of the sample, and to have references for molecularly dispersed stabilisers as well as sophisticated calculation for the obtained spectra. On the other hand, broad-band dielectric spectroscopy [19-22] can be applied to investigate solubility and compatibility, as it offers an excellent possibility of detecting the molecular reorientation of stabiliser molecules and segments simultaneously at the same temperature. Accordingly, the degree of compatibility with most polymeric segments can be evaluated, where detailed investigation of the molecular dynamics have been carried out [19-22] for various additives having different shapes, sizes and polarities in different polymeric matrices.

An empirical relation that determines the dependence of the relaxation frequency differences between the cooperative process of the additive and the glass process of the matrix (macro-Brownian cooperative reorientation of the segment associated with the glass temperature) and the additive length has been given [21]:

$$\Delta \log f_m = 4 \log[(L/d) - 1] \quad (10.6)$$

where $\Delta \log f_m$ is the difference between $\log f_m$ of the cooperative process of the additive and $\log f_m$ of the glass process of the matrix; L is the length of the additive; and d is the

with xenon (Xenotest) and UV-B fluorescent tube (QUV Weatherometer) sources under controlled temperature and humidity conditions. The structural changes during combined photo- and thermal degradation have been studied using tensile tensiometric, IR spectrophotometric and DSC methods. The effects of HALS and film thickness on the time-dependent changes in elongation, carbonyl group concentration, crystallinity and the onset temperature (T_{on}) of the post-fusion DSC oxidation exotherm have been observed. Photooxidation is accompanied by increased crystallinity, which maximises as mechanical properties start to deteriorate significantly and the rate of carbonyl group formation increases. While there is a poor correlation between the reduction in mechanical properties and increased carbonyl index values, the former correlates well with the DSC-derived T_{on} values for unstabilised and stabilised films. This suggests that thermal analysis may be used to detect the physicochemical changes occurring in exposed films more effectively than other techniques such as IR.

However, many problems of premature film failure can occur during their use in greenhouses, due to their interaction with the agrochemicals used. Both sulfur- and chlorine-containing agrochemicals inhibit the functioning of HALS, and can have a very detrimental effect on the life of greenhouse films [25, 26].

The concentration of HALS in LDPE covering films before and after exposure to natural weathering and accelerated photooxidation conditions has been determined [27]. It has been found that photostabiliser disappearance above 0.4% up to 600 days is mostly probably the result of its physical loss during long photooxidation times under both photooxidative conditions. On the contrary, photostabiliser disappearance in the initial stage is due to chain scission and the consequent volatilisation and diffusion of these fragments on the surface.

10.5 Other Factors Affecting the Stability of Greenhouse Films

10.5.1 Temperature

Cyclic temperature changes and the high temperatures developed at the metallic parts of greenhouse constructions during hot and sunny days lead to increased degradation. One can observe a lot of damage in the places where the plastic greenhouse films come into contact with the metallic structural elements, especially when they are not painted. The temperature at these contact points may reach up to 70 °C and more depending on climatic conditions. In this case the diffusion of metal ions enhances the degradation process.

Metal particles, especially iron, may catalyse the decomposition of hydroperoxides formed as a result of oxidation, leading to unnecessarily high rates of degradation. The degradation

mechanism of PE films containing additives with metal ions at a simulated composting temperature has been studied. The hydroperoxide concentration [POOH] in the films was traced quantitatively by using iodometric potentiometric titration, and compared with Fourier transform infrared spectrometry (FTIR). The results show that [POOH] increases during the early stage of degradation, followed by a more or less flat maximum, before it starts to decrease. At the same time, similar results are obtained by FTIR analysis. It is also found that the rate laws for the carbonyl index and [POOH] increases seem more complicated than an exponential-type increase in the early stage of oxidation [28].

Moreover, high temperatures lead to an increase in the rate of reaction for both photooxidation and chemical oxidation by agrochemicals, and thus to higher degradation rates. As mentioned before, HALS compounds act as radical traps, and consequently they also act as heat stabilisers and minimise the effects of high temperature [29].

10.5.2 Humidity

Lower resistance to oxidation and enhancement of degradation occur as a result of increased humidity as well as rainfall. This is due to the gradual washout of additives that may bloom on to the surface of plastic films. Besides, the degradation of plastic films may occur due to hydroxyl radicals or other reactive species generated as a result of photolysis [30].

10.5.3 Wind

It has been suggested that tearing due to high winds can be a major problem in greenhouses. Another problem connected with windy areas is the wind load. This load can impose increased stress on plastic films and lead to premature failure of the film. Abrasion caused by soil and other particles, which are carried by the wind and impinge on the surface of the greenhouse film, may also be another problem.

10.5.4 Fog Formation

The term 'fog' is used to describe the condensation of water vapour in the form of small discrete droplets on the surface of transparent plastic films. The physical conditions that lead to this formation may be summarised as follows [31]:

- (1) A fall in temperature of the inside surface of the film to below the dew point of the enclosed air/water vapour mixture;

- (2) Cooling of the air near the film to a temperature at which it can no longer retain all the water vapour, so that excess water condenses upon the film;
- (3) The difference between the surface tension of condensed water and the critical wetting tension of the film surface, which causes the water to condense as discrete droplets, rather than as a continuous film.

A number of undesirable effects may result from fog formation in greenhouse films and leads to the following:

- (1) Light transmission will be reduced where the total internal reflection of incident light occurs. Consequently, the rate of plant growth will reduce, crop maturity is delayed and the crop yield decreases;
- (2) Light and heat transmission may be focused on delicate plant tissues owing to water droplets acting as lenses. This causes burning of the plants and crop spoilage.

To prevent fog formation, surface-active agents are usually added to PE during film production. These compounds are incompatible with the polymer and subsequently migrate to the film surface where they increase the critical wetting tension. The result is reduction in contact angle between water and polymer surface, permitting the water to spread into a more uniform layer [31].

10.5.5 Environmental Pollution

Atmospheric pollution, such as nitrogen oxides, sulfur dioxides, hydrocarbons and particulates, can enhance the degradation of polymers [32] and must also be taken into consideration. For instance, infrared studies have revealed that polyethylene reacts with NO_2 at elevated temperature and that chemical attack is observed even at 25 °C. Similarly, SO_2 is rather reactive, especially in the presence of UV radiation, which it readily absorbs and forms triplet excited sulfur dioxide. This species is capable of abstracting hydrogen from polymer chains, leading to the formation of macroradicals in the polymer structure, which in turn can undergo further depolymerisation [33].

10.5.6 Effects of Pesticides

The use of agrochemicals in greenhouses severely affects polymer films [29]. The pesticides used for the protection of the crop influence the degradation and lifetime of the films. Usually pesticides have complicated formulations, and contain a number of compounds besides the active component. They contain sulfur and halogen in their chemical structure. It is a well-known fact that films are destroyed under the effect of pesticides.

Pesticides react with the stabilisers present in the film, decreasing its effect or completely destroying it. Experimental results clearly show that pesticides with sulfur-containing active compounds enter into antagonistic interaction with the stabilisers. One simple explanation [34] is that the interaction of the pesticide and the HALS compound prohibits the latter in executing its effect. Some sulfur-containing compounds and organic halogenides initiate the oxidation of PE and bring about rapid deterioration of its mechanical properties. The extent of this negative effect depends on the molecular weight, dispersion, allotropic modification, etc., of the elementary sulfur. The introduction of a UV absorber into film considerably improves the lifetime and light stability of the film. Also, HALS-stabilised greenhouse films were shown to last 33% longer than Ni-stabilised films in testing under real conditions.

However, the polymer materials used for greenhouse films are changing, and, in particular, the use of blends is continuously increasing, like the use of additives. These additives are used in relatively large amounts for different aims, like photooxidation resistance, anti-fogging, etc. Moreover, the films can absorb fertilisers and pesticides, which can compromise the use of secondary materials coming from greenhouse covering films in many applications. UV exposure gives rise to major modifications of the macromolecular chains, with chain breaking, formation of oxygenated groups, possible formation of branching and crosslinking, and so on [35-38]. Finally, the reprocessing operations can induce further degradation due to the thermomechanical treatment in the melt [39-42].

10.6 Ageing Resistance of Greenhouse Films

10.6.1 Measurement of Ageing Factors

Evaluation of the stability and durability of greenhouse films is usually carried out using laboratory equipment. There is no standard testing scheme for evaluating the degradation of these properties when the plastic film is used as a greenhouse covering material. This is due to the fact that there are several interconnected factors that can lead to the degradation of the mechanical properties. These factors are usually difficult to realise in the laboratory. Following up the changes that occur in the mechanical properties of plastic films as a result of ageing is very important in order to throw some light on the problem and to identify the conditions of the film. However, other properties of the film, such as physical and chemical properties, are also affected by the degradation, e.g., abrasion directly affects light transmittance and also other mechanical properties.

Many research groups have paid attention to this problem and concentrated their efforts on measuring the effects of various ageing factors on the degradation of plastic materials [6, 43, 44]. Some of them are concerned with the very specific problem of ageing of agricultural plastic film [24, 45].

In principle, all parameters should be covered in order to be able to predict accurately the performance and lifetime of the material under the particular circumstances that would occur when the material is used in a greenhouse. The accelerated ageing process consists of simulating in an intensified manner the most critical parameters that lead to the degradation of plastics. Several accelerated ageing tests for plastic films have become commercially available during the past decade. However, their relationship to real outdoor ageing is extremely questionable. These tests are based on inducing artificial ageing in the material through an intense UV source coupled with a day-night cycle and a water spray cycle. Only a few studies have considered the use of pesticides or stress due to wind loading combined with the effect of UV-induced ageing [25]. An empirical correlation between the lifetime of films under artificial weathering and in the greenhouse situation has been given [46]. This standard defines three climatic zones depending on the level of solar radiation energy that they receive: 70-100, 100-130 or 130-160 kLy/yr, where the kilolangley is given by 1 kLy = 4.184 kJ/cm².

However, no special conditions – such as the contact between the film and the metal parts of the greenhouse structure, and the application of pesticides that can strongly influence the actual weathering of the plastic films – have been considered. Thus, the artificial ageing tests can only provide a rough estimate of the actual behaviour of plastic films when exposed to the real and complicated environmental factors that affect the plastic during its use [47]. For this reason several researchers have studied the degradation of plastic films under natural weathering conditions (outdoor tests) [48]. Only a limited number of tests were performed in greenhouses by this group [48].

10.6.2 Changes in Chemical Structure

Changes in chemical structure resulting from plastic film ageing have been followed using spectroscopic methods. FTIR is the most frequently used technique [47, 49]. It provides information about the chemical structure of the macromolecules. For instance, when the chains are oxidised, carbonyl and OH groups are formed. The additive concentrations and their changes can also be detected by the same technique. The presence of parts of the agrochemicals in the film can also be detected spectroscopically. Electron spin resonance (ESR) is also used to detect the creation of free radicals during degradation [49].

Thermal analysis, such as DSC, is used to study the oxidation process as well as the changes in the crystallinity of plastic films due to ageing [50].

Gel permeation chromatography (GPC) may be used to evaluate the changes in the molecular weight and molecular weight distribution of the films [8]. The integrated area between 1770 and 1690 cm⁻¹ of the absorption band at 1734 cm⁻¹ was used to determine the concentration of Tinuvin 622 [poly(N-β-hydroxyethyl)-2,2,6,6-tetramethyl-4-

hydroxypiperidyl succinate)] before and after film exposure. The oxidation degree, i.e., carbonyl index (CI), under different oxidation conditions was obtained by calculating the carbonyl absorption at 1713 cm⁻¹ from the FTIR spectra at various oxidation times using the spectrum of the unoxidised starting material as a reference. All measured absorbances should be normalised by the film thickness using the equation:

$$CI = (A_{1713}/d) \times 100 \quad (10.7)$$

where A_{1713} is the measured absorbance at 1713 cm⁻¹ at a certain exposure time, and d is the film thickness in micrometres.

10.7 Recycling of Plastic Films in Agriculture

10.7.1 Introduction

The amount of plastic materials used in agriculture has been continually increasing. Plastic materials are used for greenhouse covers, mulching, piping, packaging and other applications. Films used for greenhouses can be considered as an easy source of materials for recycling. Indeed, large amounts of film can be easily collected and, because of the homogeneity of the polymers used for this application, the recycling operations can be relatively easy. However, UV exposure gives rise to major modifications of the macromolecular chains, with chain breaking, formation of oxygenated groups, possible formation of branching and crosslinking, and so on [35, 36, 51, 52].

The recycling of post-consumer films for greenhouses is strongly dependent on the initial structure of the plastic materials and on the processing conditions. Such films contain small amounts of low molecular weight compounds probably coming from the photooxidation of the PE molecules and from the absorption of fertiliser and pesticide residues. The amount of these compounds is small, however, and does not prevent the use of the recycled materials in many applications. The properties of the secondary materials deteriorate with the number of extrusion steps, but especially with the increasing extent of photooxidative degradation. However, the mechanical properties of the recycled post-consumer film remain relatively good even after many extrusion passes, and such film is useful for many applications [53].

10.7.2 Contamination by the Environment

Dow Chemicals have actively investigated the recycling of mulch film because the normal practice of disposal by burning it on the fields is environmentally undesirable. The

contamination levels in mulch film make its recycling particularly challenging. For instance, soil contamination can be as high as 30-40%. Furthermore, the soil can contain up to 3% iron, which is a polyethylene prodegradant [54]. In addition, it was found that vegetable matter derived from harvested plants could not be removed during the washing operations [54]. Other contaminants are fumigants, (e.g., methyl bromide), and the oxidised fractions of LDPE resulting from photodegradation of the mulch film.

Recently effort has been focused on the recycling of LDPE mulch film and greenhouse film, both of which contain pesticide residues. This area poses special problems that are difficult to overcome. It has been discovered that organochlorine and organosulfur pesticide residues can deactivate HALS. This deactivation is believed to occur as a result of hydrolysis of the pesticides to acidic species that then react with the HALS. This has implications with respect to the long-term outdoor stability of the recycled product.

During in-service use, PE can become badly degraded and can form low molecular weight oxygenated products, (e.g., aldehydes, acids, ketones, waxes, etc.). These impurities can lead to embrittlement of the recycled polymer because low molecular weight oxidised fractions are segregated from the melt during crystallisation and concentrate at the spherulite boundaries [55]. The resulting zone, rich in oxidised material, has very low fracture toughness. Moreover, oxygenated degradation products of PE, such as carbonyl groups, are active chromophores and can sensitise the reprocessed polymer to photodegradation.

Plastic waste management, in general, is a global environmental problem. The management of such waste may be through the famous 4R approach:

- Reduction (of source material);
- Reuse;
- Recycling;
- Recovery.

The recycling and reuse of plastic waste films generated from greenhouses can share in solving the problem. The disposal of municipal solid waste has become an environmental issue of growing concern [56]. It was determined that discarded plastics represent close to 20% of municipal solid waste on a volume basis [57, 58]. This is due to the high volume-to-weight ratio of polymeric materials.

The management of plastic waste follows the scheme:

- Source reduction;
- Recycling;

- Thermal reduction by incineration;
- Land-filling.

The most feasible methods for developing countries are source reduction and recycling. Source reduction is any measure that reduces the volume of plastic waste produced. This is accomplished through material efficiency, i.e., reducing the quantity of plastic material used to produce a particular item.

Recycling generally involves the collection of waste plastic materials for reprocessing [59, 60]. Polyolefin blend technology is of critical importance to various applications, including greenhouse films. For instance, the LLDPE/LDPE blend is characterised by reduced haze and better bubble stability. One of the most common blends is LDPE/ethylene-propylene-diene terpolymer (EPDM) with improved low-temperature flexibility, rubbery properties, weathering resistance and high-temperature mechanical properties. The addition of EVA to LDPE has been commercially utilised to improve environmental stress cracking resistance, toughness, film tearing resistance, flexibility and optical properties.

Both blending and coextrusion have been employed to deal with the problem of agricultural plastic film waste. The main goal is to find a solution to the problem of agricultural plastic waste from greenhouses by recycling and converting the waste into products usable in the mulch and greenhouse film applications. The proposed solution is based on the development of multilayer films consisting essentially of a top layer made from virgin resin and a bottom layer consisting of a blend of recycled PE waste film material in combination with virgin resin and other ingredients. Evaluation of greenhouse plastic wastes revealed that it is possible to obtain useful transparent plastic films to be reused with reduced cost [61].

Multilayer films for greenhouses are a current trend in the industry. LDPE films for the top layer, stabilised with different concentrations (0.1, 1.0 and 2.5%) of UV quencher, have been produced in the laboratory by blow extrusion. The effect of natural weathering on the film properties was investigated over a period of 12 months [62]. Significant changes in the mechanical properties were observed in the later stages of degradation. Films stabilised with 0.1% stabiliser crumbled after 12 months of natural weathering, whereas films with higher concentrations retained their mechanical properties. It is believed that the inclusion of a UV stabiliser interferes with the crystallisation process and that the stabiliser particles accumulate in the amorphous matrix. Degradation of the imperfect crystalline region with its low oxygen permeability proceeds via crosslinking, whereas chain scission predominates in the amorphous region with excess of oxygen. Films stabilised with 2.5% UV quencher form a barrier against the transmission of UV radiation and the bottom layers are less affected by UV radiation. Recycled material can, therefore, be incorporated at high concentrations into these layers.

Optimisation of the top layer was based on a fixed concentration of three thermoplastics, i.e., 80% LDPE, 10% LLDPE and 5% EVA, the remaining 5% being a specially prepared master batch of LDPE containing 25% UV and heat stabilisers. Different types of UV stabilisers were taken in different concentrations. These are: Cyasorb 1084 [*n*-butylamine-nickel-2,2'-thio-bis(4-*tert*-octyl phenolate)] and Chimassorb 81 [2-hydroxy-4-*n*-octoxybenzophenone], acting as UV light absorbers; Chimassorb 944 LD [poly[6-(1,1,3,3-tetramethylbutyl)imino-1,3,5-triazine-2,4-diyl amino-hexamethylene-4-(2,2,2,6-tetramethylpiperidyl)imine]] and Tinuvin 622 LD, acting as radical scavengers; an energy transfer agent; and a peroxide decomposer. The data obtained show that the haziness of all plastics films are within the range required for agricultural films.

It has also been found in the case study [62] that the utilisation of a single UV stabiliser is less efficient than the utilisation of a two- or three-component UV stabiliser. Thus, films containing three-component UV stabilisers in addition to a thermal stabiliser (Irganox 1076) can retain at least 94% and 81% of tensile strength and elongation at break, respectively, after exposure to UV radiation for 600 h. The good resistance of these plastic films can be attributed to the different mechanisms of action of the utilised stabilisers. In other words, if the UV absorber Chimassorb 81 is added alone to the plastic blend, the films retain about 63% of the original elongation; whereas in combination with Cyasorb 1084, the retained elongation is increased to about 80%. Consequently, these results indicate the necessity of using a combination of UV absorbers and radical scavengers [62]. Furthermore, some plastic films of various compositions were subjected to outdoor weathering tests in two different locations, Cairo and Upper Egypt. The results obtained indicate that the unprotected films deteriorate completely within three months, whereas the protected films can withstand almost one year without a drastic decrease in mechanical properties.

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11

Physicochemical Criteria for Estimating the Efficiency of Burn Dressings

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11.1 Introduction

The principal medical treatment of burns is the use of dressings, which often worsen the effects of the injury. It is difficult to estimate the effectiveness of new burn dressings, as their physicochemical properties are not usually presented in the literature. This chapter is devoted to a discussion of this subject for the first time. The authors address the complexity of physicochemical methods of analysis in order to create criteria for efficient dressings for a burn wound surface. The characteristics typical of burn wounds for which dressings are required are shown in Table 11.1.

Table 11.1 Characteristics of burn wounds [3]			
Burn degree	Image of damage	Physiological process	Burn depth (mm)
I	Redness and oedema (medium oedema)	Aseptic inflammatory process	0
II	Sac formation	Aseptic inflammatory process	0
III	Damage of skin cover, exuding wound surface	Skin necrosis, tissue necrosis	1-2
IV	Exuding wound surface	Full necrosis of tissues, carbonisation of tissues	2-5

Based on theoretical and experimental data, it was found that the maximal sorptional ability of a burn dressing is determined by the free volume of the dressing material calculated from the value of the material density. Kinetic parameters were determined from the sorption curves. These parameters help in predicting the behaviour of burn dressings. Criteria for estimating the efficiency of first-aid burn dressings are then formulated.

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13

Recycling of Plastic Waste

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13.1 Introduction

Polymeric materials (plastics and rubbers) comprise a steadily increasing proportion of the municipal and industrial waste going into landfill. Owing to the huge amount of plastic wastes and environmental pressures, recycling of plastics has become a predominant subject in today's plastics industry. Development of technologies for reducing polymeric waste, which are acceptable from the environmental standpoint and are cost-effective, has proven to be a difficult challenge, because of the complexities inherent in the reuse of polymers. Establishing optimal processes for the reuse/recycling of polymeric materials thus remains a worldwide challenge in the new century.

Compared with other countries, there is a huge amount of plastic waste in the USA (taken as a reference), where five main types of polymers dominate in the plastics waste stream. The highest polymer waste results from low-density polyethylene (LDPE), at 5 million tons per year; high-density polyethylene (HDPE) is second, at 4.1 million tons; then come polypropylene (PP) at 2.6 million tons, followed by polystyrene (PS) at 2 million tons and polyethylene terephthalate (PET) at 1.7 million tons [1]. These five polymer types, together with polyvinyl chloride (PVC), also dominate the plastics waste stream in the European Community [2].

Plastic films find applications in agriculture as well as in plastic packaging, which is a high-volume market owing to the many advantages of plastics over other traditional materials. However, such material is also the most visible in the waste stream, and has received a great deal of public criticism as films have comparatively short life-cycles and usually are non-degradable [3].

The majority of plastic films are made from LDPE or linear low-density polyethylene (LLDPE), comprising approximately 68% of the total film production. In addition, HDPE resins are commonly used in film plastics. Non-polyethylene resins constitute the remainder of the film plastic types found in the market place. PP, PVC and Nylon resins comprise the bulk of these other film types. Increasingly, certain multilayer or coextruded films are used in special applications that seek to combine the performance attributes of two or more resins for such applications.

Businesses can save money by reducing their disposal expenses, in the form of both tonnage-based tipping fees and container hauling fees. This is especially evident with plastic films, where a high volume-to-weight ratio can mean more container pulls per ton hauled.

13.2 Main Approaches to Plastic Recycling

There are four main approaches to recycling plastics (excluding, as not acceptable, dumping on land or at sea with or without prior treatment) [4]. These are primary, secondary, tertiary and quaternary recycling.

13.2.1 Primary Recycling

This is the recycling of clean, uncontaminated, single-type waste, and it remains the most popular as it ensures simplicity and low cost, especially when done 'in-plant' and fed with scrap of controlled history [5]. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as second-grade material [6]. Primary recycling is very simple without any precautions except the proper and clean collection of the waste in the plant.

13.2.2 Secondary Recycling

13.2.2.1 Approaches to Secondary Recycling

There are two main approaches to secondary recycling. One approach is to separate the plastics from their contaminants and then segregate the plastics into generic types, one or more of which is then recycled into products produced from virgin or primary recycled material. The other approach is to separate the plastics from their associated contaminants and remelt them as a mixture without segregation. The treatment of the plastics-containing waste streams may include: size reduction by granulators, shredders or crumblers; separation of plastics from other waste materials and from one another; cleaning; drying; and compounding [7, 8]. The actual order and number of operations in a particular treatment system depends on the waste being processed and the desired quality of the final material [9].

13.2.2.2 Mechanical Recycling

Mechanical recycling is mainly related to secondary recycling. The main steps include separating, sorting and washing to get rid of contamination, especially for plastic films,

which possess a large surface area and consequently have a large degree of contamination. In a chemical recycling plant, one should have shredders, metal and mineral separators, prewashing and granulation, second washing stage, mechanical grinding and dirt removal, hydrocyclone separation, dewatering and melt processing.

The separation of plastic waste is one of the main factors restricting high performance in plastic recycling. The separation of plastics into desired categories as well as the elimination of contaminants is an ongoing technological development process. The aim is to develop automatic and continuous separation technology to minimise the handling of waste and to achieve a more efficient recycling process. Probably the best alternative for pure plastic streams is not to allow them to mix in the first place, neither among themselves nor with contaminants. If separation starts at the consumer level and at the source point of collection, there will be fewer difficulties during the recycling.

13.2.3 Tertiary Recycling

Tertiary recycling includes chemical recycling. The terms 'chemical recycling' and 'feedstock recycling' of plastics are sometimes collectively referred to as 'advanced recycling technologies'. In these processes, solid plastic materials are converted into smaller molecules as chemical intermediates through the use of heat. These chemical intermediates, usually liquids or gases, but sometimes solids or waxes, are suitable for use as feedstocks for the production of new petrochemicals and plastics.

The technical and economic feasibility and overall commercial viability of advanced recycling methods must be considered in each step of the recycling chain, consisting of collection, processing and marketing. All of them are critical to the success of chemical and feedstock recycling. Today, most of these technologies remain developmental and have not yet proven themselves sustainable in a competitive market. Nevertheless, they remain of considerable interest in their longer-term potential.

The term 'feedstock recycling' encompasses chemical recycling but is often applied to the thermal depolymerisation of polyolefins and substituted polyolefins into a variety of smaller hydrocarbon intermediates. Fluidised bed pyrolysis investigations of LDPE have provided data on the suitability of the process and on the influence of the process conditions on the compatibility of the feedstock produced with the conventional petroleum feedstock [10]. The gases produced from the pyrolysis of LDPE are mainly hydrogen, methane, ethane, ethylene, propane, propene, butane and butene. Also, it has been reported that the thermolysis products of HDPE consist of 80-90 wt% straight-chain alkanes and 1-alkenes. Subsequent hydrogenation of the PE oil resulted in a diesel fuel with high cetane index and low sulfur and aromatic contents [11].

and by considering all proper means to avoid pollution. The costs of operating, maintaining and monitoring an incinerator are quite substantial compared to those for a conventional power plant. Energy from waste (EFW) is a reliable and renewable source of energy, especially if the MSW is rich in organic matter. Furthermore, it reduces the amount of waste to be landfilled at the final stage. Costs involved in developing new landfills can partly offset the high costs of energy recovery from an EFW facility. Incinerators with EFW installations are not considered just as power plants, as their main purpose is to reduce the amount of garbage being landfilled within the purpose of an integrated waste management system.

Incineration plants should be designed and operated to produce the least amount of pollution. The use of incineration plants is mandatory for plastic wastes from hospitals and similar institutions, which is considered as a potential source of disease. Incinerators do not emit ethane gas, as this gas is completely combusted into CO₂ and water, even at low temperature. However, incinerators have often been associated with dioxin and furan emissions, which are avoided in modern ones by working at temperatures that are high enough to decompose such chemicals and prevent them from reaching the ecosystem. Although dioxin and furan are often perceived as two individual chemical products, there are in fact 75 congeners of polychlorinated dibenzodioxins (PCDD) and 135 congeners of polychlorinated dibenzofurans (PCDF), each differing in its chemical configuration and degree of toxicity. The most toxic of the dioxins is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). When assessing health risks, the total congeners are converted to the equivalent TCDD. Dioxins and furans are present in Nature and are generated by many sources, such as forest fires and as a by-product of a certain chemical processes and the burning of wood in stoves and fireplaces, barbecues, diesel engines, power plants, ponds and so on. Scientists can account for about 60% of the dioxins found in Nature (referred to as 'background level'), while the source of the remainder is still unknown. Dioxins enter the human body through the food chain, inhalation and skin contact. As long as the quantities absorbed are very minute, however, they do not represent a health hazard.

The complete combustion of organic matter removes all the dioxins present in the garbage. However, during cooling of the flue gases, traces of dioxins are formed. An energy-from-waste facility acts as a reliable and renewable source of energy. It is a safe method of reducing the volume of waste dumped in landfills. A considerable reduction in the emission of greenhouse gases compared to landfills can be achieved. However, further research is needed to avoid completely this emission.

Recovery of energy from solid waste constitutes the fourth 'R' after reducing, reusing and recycling. Research as the fifth 'R' is the key element. Scientists and environmental scientists have to work together to develop new methods for recycling more products.

In some cases, addition polymers such as polystyrene and polymethyl methacrylate can be thermally depolymerised back to their corresponding monomers in reasonably high yield. The term 'chemical recycling' is often applied also to the depolymerisation of certain condensation polymers back to monomers. Examples of these types of plastics are polyesters, polyamides and polyurethanes. Chemical recycling thus mainly includes pyrolysis, gasification, hydrogenation, hydrolysis, glycolysis and depolymerisation.

A new reactor system was developed for the recovery of fuels from waste plastic mixtures in a steam atmosphere. The degradation mechanisms of two polyolefins (PE and PP), two polyamides (Nylon-6 and Nylon-6,6), polystyrene and three polyesters (polycarbonate, polybutylene terephthalate and polyethylene terephthalate) in both nitrogen and steam as the carrier gas have been investigated [12]. The oil produced from the proposed reactor system was continuously upgraded to produce gasoline and kerosene over a Raney nickel catalyst in a steam atmosphere.

13.2.4 Quaternary Recycling

Quaternary recycling includes the recovery of the energy content of plastic wastes. Owing to a lack of other recycling possibilities, incineration (combustion) aimed at the recovery of energy is currently the most effective way to reduce the volume of organic material. This may then be disposed of to landfill. Plastics, either thermoplastics or thermosets, are actually high-yielding energy sources. For example, one litre of heating oil has a net calorific value of 10,200 kcal, whereas 1 kg of plastics releases 11,000 kcal worth of energy; for comparison, it should be added that 1 kg of briquettes (blocks of pressed coal dust) has a net calorific value of 4,800 kcal. It has been estimated that, by burning 1 ton of organic waste, approximately 250 litres of heating oil could be saved [13]. Clean incineration of municipal solid waste (MSW) is widely accepted in countries like Sweden and Germany (50% of total MSW), Denmark (65%), Switzerland (80%) and Japan (70%) [14]. Although there are very stringent emissions regulations, more than 50 refuse incineration units are working in Germany.

The energy that can be recovered from the incineration of plastics depends on the type of plastic. It has been estimated (in kcal/kg) as: 18,720 for PE; 18,343 for PP; 16,082 for PS; 13,179 for phenol-formaldehyde; 11,362 for foamed polyurethane (PU); 10,138 for Nylon; 8,565 for polyvinyl acetate (PVAc); 7,516 for PVC; and 7,014 for PU. This energy is on average 10,000 kcal/kg. Each ton will release about 10⁷ kcal.

However, plastics emit some objectionable gases and form some hazardous compounds. Thus, recovering energy from plastic waste is not cheap. The main goal must be to avoid the formation of these hazardous compounds by the correct construction of incinerators

13.2.5 Conclusion

In conclusion, primary recycling is ideal for clean, uncontaminated single-type scrap, but degradation during service life or reprocessing should be taken under serious consideration.

Secondary recycling by type can be accomplished by various methods, but the cost associated with the separation and decontamination of the wastes undoubtedly poses an inherent obstacle. Dissolution-based techniques seem worth developing, but cannot yet be considered to be the complete answer. Secondary recycling of plastics mixtures by remelting is intended to produce downgraded products as a result of incompatibility problems. Compatibilisation is effective only in specific cases of plastics mixtures.

Tertiary or 'chemical' recycling processes involve high levels of investment and succeed in recovering the chemical products, but negate the value added during the polymerisation. The latter comment is valid also for the last resort, quaternary recycling (energy recovery of plastics waste), which can substitute other energy sources and solve disposal problems. However, it stands strongly accused of undesirable emissions.

The first and most important steps in plastic recycling are collection and sorting, after which the recycling process depends on the type of plastic and the field of application. These issues will now be addressed.

13.3 Collection and Sorting

Collection involves gathering lightweight packaging films and other materials. Plastic packaging from separate collection streams is separated from other lightweight packaging material and sorted into fractions comprising film containers, mixed plastics and residues. Identification of the plastic type is one of the most important elements in recycling because most recycling processes prohibit certain types of plastics. For example, severe problems appear during processing of recycled resin of unknown origin. Thus, extrusion and injection moulding require accurate identifications of plastic waste, otherwise a product with bad appearance and impaired quality, especially poor mechanical properties, is obtained.

13.3.1 Resin Identification

Identification has become more complicated, not only due to the presence of plastic materials compounded with additives such as plasticisers, stabilisers, flame retardants, fillers and others, but also due to the presence of polymer blends in the waste. Some time ago, the Society of the Plastic Industry (SPI) introduced a labelling system for recyclable

plastic material. It is now common for manufacturers to use this code system printed or moulded on the product surface for easy plastic identification. The code is a three-sided triangular arrow with a number in the centre and letters underneath, indicating the type of resin: 1 for PET; 2 for HDPE; 3 for vinyl polymers, especially PVC; 4 for LDPE; 5 for PP; 6 for PS; and 7 for others. It is thus easy to develop automated scanning systems that can read the SPI or other codes. This will help to identify the resin used [15]. Furthermore, separation of plastic containers has been proposed by printing bar codes on them [16].

Plastic films are more difficult to identify than plastic containers, because most films do not carry a code, and producers and recyclers need training on how to distinguish between film types. Sorting generally must occur early in the recovery process, near the initial point of generation, to be successful.

Optical systems for identification of mixed plastics have been used. A few technologies originally designed and used in the film and packaging industry were considered earlier. Electromagnetic scanning equipment was used to recognise chlorine molecules and so to sort PVC from PET [17]. An X-ray fluorescence (XRF) analyser as a photoelectric sensor was also used to identify transparent PET, green PET, translucent or natural HDPE, pigmented HDPE and PVC. The sensor system is connected to an automatic sorting line. Automation of the process reduces costs and improves the resale value of the separated plastics. Although dirt does not significantly influence the fluorescence intensity from bottles, paper labels do reduce the intensity but do not pose an obstacle in detecting vinyl bottles [17]. Paper labels are virtually blind to X-rays.

Infrared and other spectral separation devices have been reported for the continuous examination of waste products [18]. However, a satisfactory process for the identification of plastic products for commercial purposes has yet to be developed.

13.3.2 General Aspects of Resin Separation

Resin separation from contaminants or from undesired materials to obtain the desired stream can be achieved by a number of processes. These are: magnetic separation for the removal of ferrous materials; an electrostatic method for nonferrous, mainly aluminium, separation; air separation via cyclones to separate paper; and flotation tanks or hydrocyclones used to separate various resins based upon specific gravity. After that the processed materials are shredded.

Automatic separation of shredded plastic waste is very difficult if the resins have similar specific gravity. Fortunately, 85% by volume of world plastic consumption is of four main thermoplastic resins: PE, PP, PVC and PS [19]. In the next sections, some separation techniques based on different properties will be discussed.

13.3.3 Resin Separation Based on Density

Air classification can be used to separate plastics on the basis of their bulk densities; thus film and foamed plastics may be separated from heavier forms of plastic material or paper [20-22].

The densities of the major thermoplastics give the potential to separate them into types by a series of float-sink operations [23, 24]. Water may be used to separate PP, LDPE and HDPE from PS, PVC and PET. A liquid having a density of about 930 kg/m³ may be used to separate PP and LDPE from HDPE; the PP and LDPE may then be separated using a liquid having a density of about 910 kg/m³. The PS and PVC may be separated using a liquid with a density of about 1150 kg/m³ [20]. Blending or filling a plastic may change its density to the point where it could cause difficulties in the float-sink operation processes. Labels, residual adhesives, metals and metallic-plastic composites cause similar difficulties, and therefore processes have been developed to remove these contaminants before the mixed plastic materials enter a separation system [25]. As an example, a solvent washing stage, using either tetrachloroethylene- or hexane-related solvents, was added to the classic water-washing treatment. These solvents were believed to remove not only the glues but also any toxic organic chemicals that have been stored in beverage bottles by consumers or are present as additives in plastics and that inadvertently will be present in the end-products [26].

A different approach for separating mixed plastic wastes by density has been reported [27, 28]. The process uses the properties of a fluid near its critical point to allow fine separations at mild temperatures and pressures. The density of the medium can be varied over a wide range and controlled to a sensitivity of ± 0.01 g/cm³. Carbon dioxide is the most commonly used supercritical fluid and can be compressed to densities in the range of 1000 kg/m³. Since the separation of non-olefin thermoplastics will require fluid densities up to approximately 1400 kg/m³, mixtures of carbon dioxide and sulfur hexafluoride, a very dense supercritical fluid, may be used. By effecting small incremental changes of pressure, pure CO₂ efficiently separated LDPE, HDPE and PP. Separation of green PET, clear PET and PVC has also been demonstrated, and separation of light- and dark-coloured HDPE is possible. The different densities exhibited by PET in the neck and the body of PET bottles can be separated by CO₂/SF₆. The possibility of separating various components of wire and cable scrap also exists.

The centrifugal field produced in a hydrocyclone has been extensively used for the separation of plastics. In a hydrocyclone, the flow rate referred to the separation area is 100 times higher than in a static float-sink separator. The contamination of plastics is of only minor relevance in this process compared to flotation. For the separation of an *n*-component mixture, *n* - 1 separation stages (cyclone plants) are necessary.

Furthermore, continuously operated plants must be equipped with a feeding device and screens for dehydration purposes [29]. Using hydrocyclones, PS, PET and PVC can be separated from one another or from polyvinyl alcohol; polyolefins from municipal solid wastes; PET from PE, PP and paper; and PP car bumpers from metals and other contaminants [30-32].

13.3.4 Resin Separation Based on Colour

Photoelectric sensors are used for the separation of mixed, whole, or baled plastic containers. One of the systems uses mechanical means to reduce the baled plastic into individual bottles and to screen contaminants. After deballing and screening, the containers are manipulated into a single-line presentation to an optical sensor that performs a three-class identification: Class 1, dairy HDPE and PP; Class 2, PET and PVC; and Class 3, mixed colour HDPE containers. Another optical sensor can be used to discriminate green and amber PET from clear PET containers, PP from dairy HDPE containers, and mixed colour HDPE according to seven colour classifications. However, reliable identification of post-consumer containers requires that measurements from much of the container surface should be ignored. These areas include closures or necks, labels, edges, bottoms and areas with residue of dirt [33, 34].

13.3.5 Resin Separation Based on Physicochemical Properties

13.3.5.1 Electrification

The separation of mixed plastic wastes can be achieved using high-voltage drums, taking advantage of their different relative positions in the charging sequence. The process involves first tribo-electrification of the shredded plastic particles of the mixture by fluidisation. Subsequently, the electrified mixture is conveyed through an electrostatic field that separates the individual particles according to the magnitude and the polarity of the electric charges acquired during the tribo-electrification. When fluidising a mixture of two shredded plastics, the particles of the plastic with the lower work function transfer electronic charges to those with the higher work function. For example, the tribo-electrical contact between PVC and PET results in PVC having a negative charge and PET a positive charge. In the case of PET/PS mixtures, PET has a negative charge and PS a positive charge [35]. Mixtures containing more than two plastic species pose a substantial problem with regard to their charging behaviour. Also, owing to the various additives contained in different types of resin, the respective positions of the plastic species are prone to change.

13.3.5.2 Spectroscopy

Spectroscopy in the near-infrared (NIR) region of the spectrum could be a key to the rapid identification of various plastics and their subsequent recovery. By illuminating the sample with light in the near-infrared and measuring the reflected light, a so-called NIR spectrum of the material is obtained, which contains information about the molecular vibrations excited by the light energy. For example, the IR vibrational spectra of plastics show characteristic absorption bands at wavenumbers ν of 1200, 1400, 1700 and 2200-2500 cm^{-1} for CH, and at 1300-1500 and 1900-2100 cm^{-1} for OH. The NH (1500 and 2050 cm^{-1}) and the CO (1730-1740 cm^{-1}) vibrations contain the relevant spectral information for plastics. Plastic objects, such as beverage bottles, can be dropped through a vertical tube, and are identified and separated while falling. This also simulates other transportation possibilities like conveyor belts. From the performance data, it was found that identification can be achieved within 0.2 s, although several measurements were needed to avoid mistakes due to dirt or labels. The problem of transparency for satisfactory measurements could be overcome by reflectance measurements [36].

Other spectroscopic methods are also possible. The identification of several thermoplastics – such as polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), PP, PS, high-impact PS (HIPS) and PVC – can be achieved by Fourier transform IR (FTIR), based on similar principles [37]. When exposed to γ -radiation, the high molecular weight (high molar mass) molecules of PVC containing chlorine atoms emit an X-ray return signature easily visible by an XRF analyser. Polyolefins, which have much lower molecular weights, emit a lower backscattering signal that barely shows up on the XRF analyser, and so is easily identified and separated [16, 38]. Bayer have proposed a process for automatic identification and sorting of post-consumer plastics, in which fluorescent dyes were added to resins during compounding, a different one for each resin type. These dyes, having high detection sensitivity, can be added in minute quantities, and so 5 g of dye per ton of polymer were sufficient for identification by a diode device [39].

13.3.5.3 Selective Dissolution of Polymer Mixtures

Finally, it must be emphasised that solvent recycling of a single-type plastic scrap serves as a model process providing fundamental knowledge for the development of a selective dissolution process.

The principle of the selective dissolution of a single polymer in a polymer mixture can be used to separate the polymers. According to the concept of selective dissolution, one polymer could be dissolved at a time, and thus dissolution-based processes can deal with mixtures of polymers. This has an evident impact on the recycling of plastics in municipal solid

waste. Mixtures of polyolefins, PS, PVC, thermosetting plastics and natural polymers (rubbers, fibres, paper, etc.) can be separated using certain solvent systems [40]. The mixture is first treated with xylene at 5-50 °C to dissolve PS, and after separation the mixture is further heated at 90-150 °C to dissolve PE, leaving PP insoluble. The three main thermoplastics – polyolefins, PS and PVC – may be separated by dissolving them in a mixed solvent of xylene (85%) and cyclohexane (15%). From the dissolution, three separate phases could be obtained containing 99% each of the pure plastics, indicating that excellent separation can be achieved. [41]. In relevant studies, toluene, xylene and kerosene have been proposed as suitable solvents for the selective dissolution of LDPE, but the information given is very limited [42, 43]. Such selective dissolution is accomplished for each of the polymers of the mixture by heating the waste dispersion at various temperatures.

13.4 Recycling of Separated PET Waste

The worldwide production of PET is above 1×10^6 tonnes per year. With such large consumption, the effective utilisation of PET waste is of considerable commercial and technological significance. PET waste may be converted into extruded or moulded articles after repelletising it. Recently, waste PET films or sheets have been cleaned, crushed, dried and mixed with LDPE waste [44]. The obtained mix was pelletised and blow-extruded into films. The maximum concentration of PET does not exceed 20%. The films obtained were found to possess very good mechanical properties compared with LDPE only. Also, the films are expected to possess good printability due to the polar nature of PET.

PET may be depolymerised to yield raw materials for resin synthesis. Recycling of segregated waste may be possible by blending in small quantities with virgin monomer, bis(hydroxyethyl) terephthalate. However, it often lowers the quality of the final product [45]. It is therefore desirable to break down the polymer into smaller fragments or oligomers [46].

PET can also be fully depolymerised into dimethyl terephthalate (DMT). However, the regenerated DMT exhibits a significantly higher carboxyl content, adversely affecting product quality. It is more economic to convert PET into low molecular weight oligomers by glycolysis in the presence of a transesterification catalyst [47-49].

When glycolysis is carried out using ethyleneglycol, the oligomers may be directly recycled into the polycondensation stage in PET manufacture, but this also lowers the product quality. Glycolysis can be carried out using different glycols, and the oligomers can be used in the synthesis of unsaturated polyester by reaction with an unsaturated anhydride [50] or used to synthesise other polymers [51].

13.5.1 Chemical Recycling of Mixed Plastic Waste

Regarding the chemical recycling of MPW with a PVC content of up to several per cent, the process consists of two parts, a liquefaction step and an entrained bed gasifier. In the liquefaction step, the plastic waste is mildly thermally cracked (depolymerised) into synthetic heavy oil and some condensable and non-condensable gas fractions. The non-condensable gases are reused in the liquefaction as fuel together with natural gas.

The heavy oil is filtered to remove large inorganic particles. The oil and condensed gas are then injected into the entrained gasifier. Also, chlorine-containing gases from the plastic waste are fed to the gasifier. The gasification is carried out with oxygen and steam at a temperature of 1200-1500 °C [55]. The products of the process are synthesis gas (predominantly H_2/CO), pure sulfur and NH_4Cl .

13.5.1.1 Polymer Cracking Process

In the polymer cracking process, some elementary preparation of the waste plastics feed is required, including size reduction and removal of most nonplastics. The reactor operates at approximately 500 °C in the absence of air. The plastics crack thermally under these conditions to hydrocarbons, which vaporise and leave the bed with the fluidising gas. The gas has a high content of monomers (ethylene and propylene) and other useful hydrocarbons, with only some 15% being methane.

13.5.1.2 Conversion Process

The feedstock recycling process was designed to handle the recycling of mixed plastic waste supplied by the collection system. The conversion of the pretreated mixed plastic into petrochemical raw materials takes place in a multistage melting and reduction process. In the first stage the plastic is melted and dehalogenised to preserve the subsequent plant segments from corrosion. The hydrogen chloride separated out in this process is absorbed and processed in the hydrochloric acid production plant. Hence, the major part of the chlorine present in the input, (e.g., from PVC), is converted into saleable HCl. Minor amounts become available as NaCl or $CaCl_2$ effluent [56]. Gaseous organic products are compressed and can be used as feedstock in a cracker.

In the subsequent stages the liquefied plastic waste is heated to over 400 °C and cracked into components of different chain lengths. About 20-30% of gases and 60-70% of oils are produced and subsequently separated in a distillation column.

There are two distinct advantages of the process: (1) the PET waste is converted into a commercial value-added product; and (2) unsaturated polyester resins based on terephthalic acid (TPA) are obtained without the processing difficulties encountered with the use of plain TPA.

Yang and Tsai [52] degraded PET fabric waste to glycolysed product by treating the PET waste with sodium hydroxide using ethyleneglycol or glycerol as the solvent. Compared with the conventional aqueous alkaline hydrolysis, they found that the degradation rate in ethyleneglycol increases tenfold. They reported that the kinetics of the alkaline ethyleneglycol treatment show that the weight loss is linear with respect to time. They concluded that using ethyleneglycol can greatly shorten the treatment time to achieve results similar to those with the conventional aqueous system.

A new chemical recycling process for PET using supercritical water has been developed by Yoshiyuki and co-workers [53]. In this method, the monomers obtained from supercritical water hydrolysis are the raw materials of each polymer. The purity of the terephthalic acid obtained from PET is about 99 wt%. It was confirmed that this process has the advantage of reducing the reaction time and simplicity of the process when compared with conventional methods such as methanolysis and glycolysis.

13.5 Recycling of Separated PVC Waste

As mentioned before, most of the technologies for the recycling of plastic wastes include degradative extrusion, pyrolysis, hydrogenation, gasification, glycolysis, hydrolysis, methanolysis, incineration with HCl recovery, or input as a reducing agent into blast furnaces.

Most of these technologies are still in the research phase, or simply are not suitable for PVC-containing waste. The latter is particularly true for technologies such as glycolysis and hydrolysis, which play a role only for well-defined single-waste streams such as PET. Some of these technologies are currently generally regarded as the most feasible ones for realisation on a practical scale. However, one group of these technologies is not designed specifically for PVC waste, but deals with mixed plastic waste (MPW) in general. These technologies mainly concentrate on recovering the organic part of the MPW. They often have restrictions with regard to the maximum permissible chlorine (or PVC) input. Other technologies are designed to deal specifically with PVC waste (chlorine concentrations of well over 10%). They emphasise recovery of the chlorine fraction in a useful form. Hence, together with the competing technologies for chemical recycling, three types of technologies have been discussed [54]:

- (1) Technologies for chemical recycling of mixed plastic waste;
- (2) Technologies for chemical recycling of PVC-rich waste;
- (3) Alternatives to chemical recycling (incineration, mechanical recycling).

Naphtha produced by the feedstock process is treated in a steam cracker, and the monomers, (e.g., ethylene, propylene), are recovered. These raw materials are used for the production of virgin plastic materials. The process is carried out under atmospheric pressure in a closed system and, therefore, no other residues or emissions are produced.

In sum, the products of the process are:

- (1) HCl, which is neutralised or processed in a hydrochloric acid production plant;
- (2) Naphtha, to be treated in a steam cracker;
- (3) Monomers, (e.g., ethylene, propylene), which can be used for the production of virgin plastic materials;
- (4) High-boiling oils, which can be processed into synthesis gas or conversion coke and then transferred for further use;
- (5) Residues.

13.5.2 Chemical Recycling of PVC-Rich Waste

These processes aim to recover as much as possible of the chlorine present in PVC in a usable form (HCl or a saleable chloride salt). The two processes in question, which are discussed below, are:

- Incineration process;
- Pyrolysis process.

13.5.2.1 Incineration Process

A plant for the processing of chlorine-containing fluid and solid waste streams is used. The goal is to process the waste by thermal treatment and to produce HCl using the energy from the process itself. The plant is based on a rotary kiln and has a capacity of 45 kilotonnes per year, (i.e., not only PVC waste), with a heat production capacity of 25 MW at ca. 7500 production hours per year.

The waste is incinerated in the rotary kiln and a post-combustion chamber, directly after the rotary kiln, at temperatures of 900-1200 °C. During this treatment HCl is released and recovered. In this way a continuous production of high-quality HCl can be assured. Also, the formation of dioxins and furans can be diminished in this way, as the goal of the process is to oxidise the waste fully, so that no toxic chemicals (dioxins and furans) are formed.

13.5.2.2 Pyrolysis Process

In this process the chemical and thermal degradation of the PVC waste takes place in a reactor at low pressures (200-300 kPa) and moderate temperatures (maximum 375 °C). Chlorine generated from the PVC reacts with fillers, forming calcium chloride. Simultaneously, the metal stabilisers that may be present in PVC waste (lead, cadmium, zinc and/or barium) are converted to metal chlorides. This product consists of over 60% lead and may be purified and reused. After completion of the reactions, three main intermediate products are formed: a solid-phase product, a liquid product and a gas-phase product.

In sum the products of the process are:

- (1) Calcium chloride (<1 ppm lead), which may be used as thaw salt or for other purposes;
- (2) Coke (<0.1 wt% lead and <0.1 wt% chlorine), which may be used as fuel in a cement kiln;
- (3) Metal concentrate (up to 60 wt% lead);
- (4) Organic condensate, which may be used as fuel for the process.

To treat the PVC waste, lime and water are needed to run the process. No dioxins, chlorine, metals or plasticisers are emitted from the process. Also, there are no liquid waste streams in the process, since all streams are recycled within the system. There is a small volume of carbon dioxide gas formed by the reaction between lime/limestone and hydrogen chloride.

13.6 Recycling of Separated PE Waste

LDPE recycling is widespread, although not to the same extent as HDPE recycling. The majority of LDPE that is recycled originates from post-industrial waste such as bundle shrink-wrap used to stabilise loads on pallets as well as greenhouse films and mulch films. There is only a limited proportion of recycled LDPE that can be classified as post-consumer recycle (PCR). Contamination in recycled PE can arise from a number of sources:

- (1) From multicomponent systems that use dissimilar polymers such as PP closures, from adhesive-backed paper labels, and even through the incorporation of additives such as pigments;
- (2) During use, (e.g., by the contents of the packaging);
- (3) During collection, (e.g., owing to consumers mixing plastic types);
- (4) By the environment, (e.g., soil in LDPE mulch film); and
- (5) By reprocessing, (e.g., gels and black specks).

13.6.1 Contamination of PE Waste by Additives

The pigments used in PE mouldings and films are often based on inexpensive metal oxides. For instance, the common brown, grey and orange pigments are based on various iron oxides and hydrates that act as prooxidants/prodegradants at the high temperatures, (i.e., 220 °C), encountered during reprocessing of HDPE. Moreover, green pigments are usually based on chromium(III) oxide, which can readily catalyse the thermooxidative degradation of HDPE when present even in trace quantities. Virgin PE is usually adequately stabilised so that these catalytic compounds do not cause in-service degradation of the polymer; however, with reprocessing, the antioxidants are usually consumed and these pigments may then be able to exert their prodegradant effects [57].

The recycled polymer can also be contaminated by pigmented components in the feedstock. In the recycling of HDPE bottles by melt processing, a major effort has been directed toward producing a naturally coloured recycle stream [58]. The major barrier to overcome to reach this end is the removal of the coloured bottle caps. LDPE film is extensively used for packaging and for the production of shopping bags. These films often contain a fatty acid amide lubricant (usually *cis*-docosenamide) that can be oxidised during thermal reprocessing of LDPE film. The lubricant readily undergoes cleavage at the unsaturated site to give a series of aldehydes that have very low odour thresholds. Such contamination imparts to the recycled material a rancid odour that may restrict its application potential.

13.6.2 Contamination of PE Waste by Reprocessing

Recycling of HDPE PCR (usually milk bottles) by melt extrusion can lead to crosslinking during the thermal reprocessing stage since the antioxidant added initially (during manufacture of the polymer) is consumed [59]. Loosely crosslinked regions (known as 'gels') can act as stress concentrations in film and cause 'blow-outs' in bottles made from recycled HDPE. Another common source of contamination in recycled HDPE (as well as virgin HDPE) is 'black specks'. These are small areas of highly degraded polymer that have been carbonised owing to excessive residence time in an extruder. These 'black specks' typically occur in low-flow regions in the extruder where 'hang-ups' form. Often, such contamination may also appear yellow, brown, or amber depending on the extent of degradation. Black specks cause a major problem in the blow-moulding of natural or white bottles because they are aesthetically undesirable.

13.7 Recycling of HDPE

13.7.1 Applications for Recycled HDPE

New markets for recycled HDPE will also emerge as a result of advances in fabrication technology allowing recycled HDPE to be used in more demanding applications that are currently the domain of LLDPE and high-modulus HDPE. For instance, there is the potential use of recycled HDPE in oriented laminates for applications such as pond liners and moisture barriers. High-performance sheets are obtained by laminating oriented HDPE webs to equalise cross-web and longitudinal properties [60]. Compared to the same thickness of monolayer HDPE, the advantages are greatly improved tensile, tear and puncture strength, and doubling of the moisture barrier properties. Specialised processing equipment has been developed to handle recycled material [61, 62].

The following are some of the commercial applications of the modified recycled HDPE:

- (1) Large mouldings;
- (2) Detergent bottles are another major outlet;
- (3) Grocery sacks ('check-out' bags) are generally produced from high molecular weight (HMW) HDPE film and have a thickness in the range 15–18 µm, their most critical performance parameters being tear strength and dart impact strength.

13.7.2 Rubber-Modified Products

Recycled rubber crumb from used car tyres is another class of modifier that is finding widespread potential for blending with HDPE PCR to yield truly 100% recycled polymeric materials [44].

Profiles extruded from recycled HDPE are finding increased use in applications such as decking, fence posts, boundary stakes, road posts, railroad sleepers and similar areas, replacing wood and concrete [63]. Such applications are generally thick sections and are ideal outlets for consuming large volumes of HDPE recycle. Furthermore, they are resistant to rotting, not liable to insect attack, and do not splinter.

13.8 Recycling Using Radiation Technology

Owing to the ability of ionising radiation to alter the structure and properties of bulk polymeric materials, and the fact that it is applicable to essentially all polymer types,

In practice, a relatively small weight proportion of polymeric materials ends up as litter. In most developed societies, domestic organic waste, including plastics packaging, is disposed of in sanitary landfill or by incineration. However, burying waste is no longer an ecologically acceptable way of disposing of consumer wastes [65, 68].

Another approach aimed at the solid waste problem is the development or evaluation of biodegradable polymers [69]. These are based on a variety of natural products (often structurally modified to optimise properties), or are laboratory-made polymers with structures designed to be susceptible to enzymatic attack. A rather large effort has grown up in this area. Polymer types being studied include cellulose derivatives (such as cellulose acetate) [70], polysaccharides such as chitin [71], starch and poly(3-hydroxybutrate) [72]. A related approach to materials that break down under natural environmental conditions is the development of UV-degradable plastics, designed to decompose in sunlight should they become 'litter' [73]. Examples include a copolymer of ethylene and carbon monoxide, and modified PET.

Two different applications have emerged over the past two decades for degradable polymers. The first is where biodegradability is part of the function of the product. Examples of this are temporary sutures in the body or in controlled release of drugs, where cost is relatively unimportant. Similarly, in agriculture, very thin films of photo-biodegradable polyethylene are used to ensure earlier cropping and to reduce weed formation [65, 66]. By increasing soil temperature, they also increase crop yields and ensure earlier harvest. A major ecological benefit of mulching films is the reduction of irrigation water and fertiliser utilisation [74]. No residues must persist in the soil in subsequent seasons to make the land less productive by interfering with root growth.

The technology of biodegradable polymers, as a solution to minimising the huge amount of plastic waste, is developing. There is an ever-widening range of polymers satisfying the requirements necessary for the numerous applications for which biodegradability of the materials is essential.

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irradiation holds promise for impacting the polymer waste problem. The three main possibilities for use of radiation in this application are:

- (1) Enhancing the mechanical properties and performance of recovered materials or material blends, principally through crosslinking, or through surface modification of different phases being combined;
- (2) Treatment causing or enhancing the decomposition of polymers, particularly through chain scission, leading to recovery of either low molecular weight mixtures, or powders, for use as chemical feedstocks or additives;
- (3) Production of advanced polymeric materials designed for environmental compatibility.

An overview of the polymer recycling problem describes the major technological obstacles to the implementation of recycling technologies, and outlines some of the approaches being taken [64].

13.9 Biodegradable Polymers

The synthetic polymer industry has brought great benefits to modern society. For example, in the packaging and distribution of foodstuffs and other perishable commodities, the commercial thermoplastic polymers are hydrophobic and biologically inert, and this has made them essential to modern retailing [65].

Similarly, in agriculture, plastics have largely replaced glass in greenhouses and cloches, and they have gained a unique position in the growing of soft fruits and vegetables over very thin polymer films (mulching films) [66]. The major group of polymers used both in packaging and in agriculture are the polyolefins, which, due to their resistance to peroxidation, water and microorganisms, are durable during use.

In the 1970s, it became evident that the very technical advantages which made polymers so useful were disadvantages when polymer-based products were discarded at the end of their useful life and in particular when they appeared as litter in the environment. Some items of plastics packaging waste were found to have very damaging effects on wildlife [67], and this led to calls from the 'Green' movement to return to biologically based (renewable) polymers.

Materials made from naturally occurring or biologically produced polymers are the only truly biodegradable 'plastics' available. Since living things construct these materials, living things can metabolise them.

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Abbreviations and Acronyms

AA	Acrylic acid
ABS	Acrylonitrile-butadiene-styrene
AC	Acetyl cellulose
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
APB	Ammonium pentaborate
APP	Ammonium polyphosphate
aPP	Atactic polypropylene
ASTM	American Society for Testing and Materials
ATH	Alumina trihydrate
au	Arbitrary units
BDD	Brominated dibenzodioxin(s)
BDF	Brominated dibenzofuran(s)
BF	Branch frequency
BFR	Brominated flame retardant
BMP	2,6-di- <i>tert</i> -butyl-4-methylphenol
BOPP	Biaxially oriented polypropylene
BPE	Branched polyethylene
BTPC	Benzyl triphenyl phosphonium chloride
BUR	Blow-up ratio
CDD	Chlorinated dibenzodioxin(s)
CDF	Chlorinated dibenzofuran(s)
CI	Carbonyl index
DBM	Dibenzoylmethane
DIN	Deutsches Institut für Normung
DMA	Dynamic mechanical analysis

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