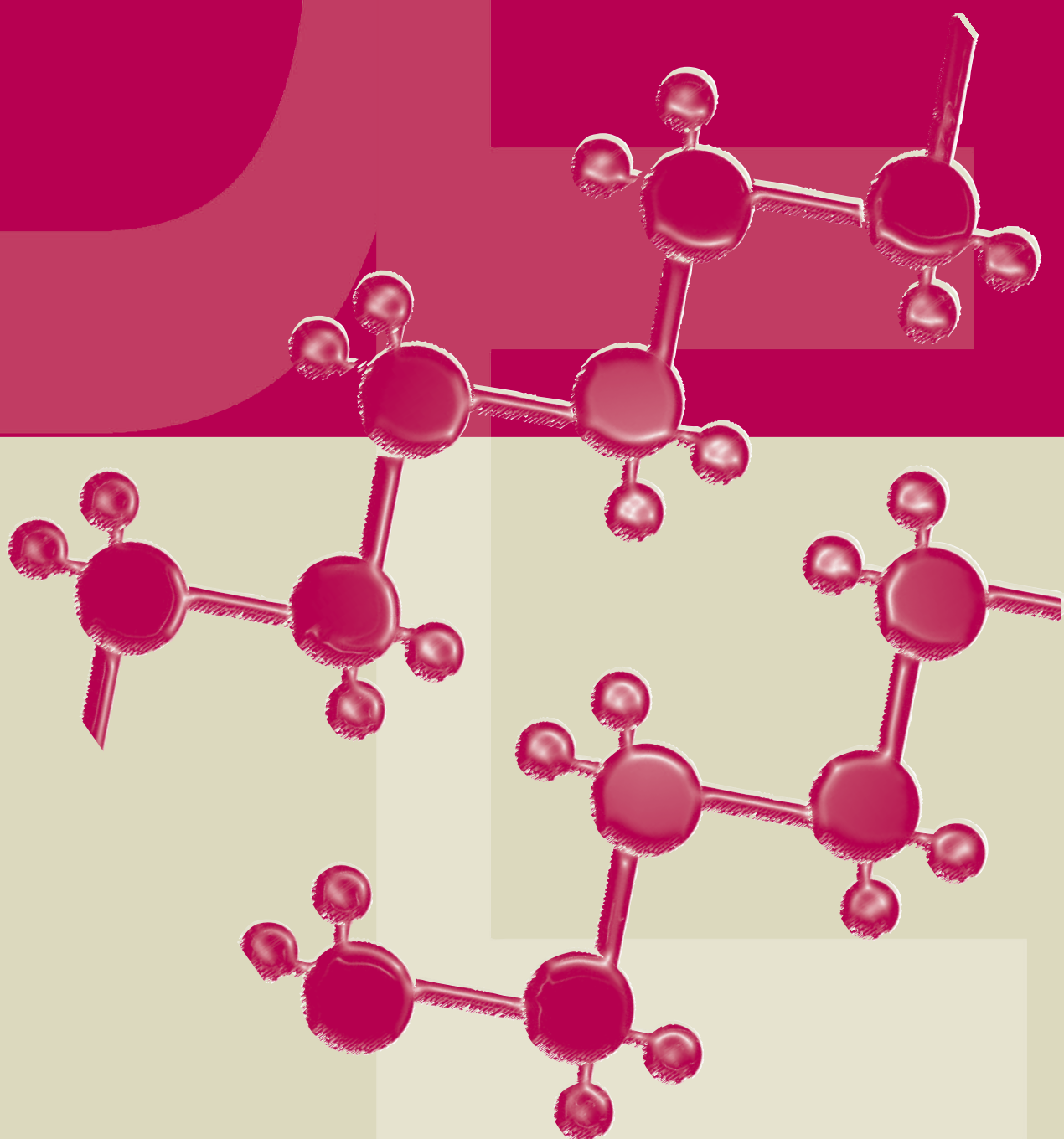


Practical Guide to Polyethylene **Practical Guide to Polyethylene**

by **Cornelia Vasile
Mihaela Pascu**



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rapra
TECHNOLOGY

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Preface

Practical guides for commercial polymers should offer the most useful information both for technological and theoretical purposes. In view of these aims, we have written this book summarising the data on commercial polyethylenes, their synthesis and processing procedures and their recommended parameters and also on the molecular characteristics of polyethylene chains including investigation methods. Because of the wide variety of polyethylene grades the task was difficult and we will be indebted to all readers making constructive comments to improve and enrich the book's content.

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1 Introduction

Polyethylene (PE) (sometimes known as polythene) was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant, Imperial Chemical Industries (ICI). Although it is more than 70 years since it was first produced, it is still a very promising material. This widely used plastic is a polymer of ethylene, $\text{CH}_2=\text{CH}_2$, having the formula $(-\text{CH}_2\text{CH}_2-)_n$. It is produced at high pressures and temperatures in the presence of any one of several catalysts, depending on the desired properties of the end-use product. Other structures (leading to long and short branches) may be present, depending on the procedure used in the synthesis. PE is the largest volume polymer consumed in the world. It is a versatile material that offers high performance compared to other polymers and alternative materials such as glass, metal or paper.

1.1 Polymerisation Processes [1]

Despite ethylene's simple structure, the field of PE is a complex one with a wide range of types and many different manufacturing processes, which offer the possibility of a versatile tailor-made range of products.

The polymerisation processes are classified with respect to the physical state of the medium, namely in suspension, in solution, in gaseous phase, and in bulk, and with respect to the reactor type, as in autoclave, tubular, loop, or fluidised bed (Table 1.1). The first three processes occur at low pressure (~10 MPa) by a coordination mechanism, while the last one occurs at high pressure (~100 MPa) in the presence of free radicals. The evolution of catalyst technology and reactor design has allowed producers to obtain polymers that improve the performance of end-use products. Recently, there have been introduced both new concepts for PE manufacture as well as the use of combined processes, such as Borstar of Borealis, giving increased product versatility. Each process presents advantages and disadvantages with respect to energy consumption, expense, and so on [2].

PE properties may be tailored by adjusting the polymerisation method or the reaction conditions (Figure 1.1). The polymer chain length and degree of crystallinity and hence the mechanical

Product	Process				
	Autoclave, high pressure	Tubular, high pressure	Gas phase, fluidised bed	Autoclave/loop, suspension	Autoclave, solution
Low-density PE (LDPE)	+	+	–	–	–
Linear low-density PE (LLDPE)	+	0	+	0	+
Very-low-density PE (VLDPE)	+	0	+	–	+
High-density PE (HDPE)	0	–	+	+	+
High-molecular-weight HDPE (HMWHDPE)	–	–	+	+	–
Ultra high-molecular-weight PE (UHMWPE)	–	–	0	+	–
Ethylene–vinyl acetate (EVA) copolymer	+	+	–	–	–
Acrylic copolymer	+	+	–	–	–

+: adequate
 0: technically possible with limitations
 –: inadequate or impossible

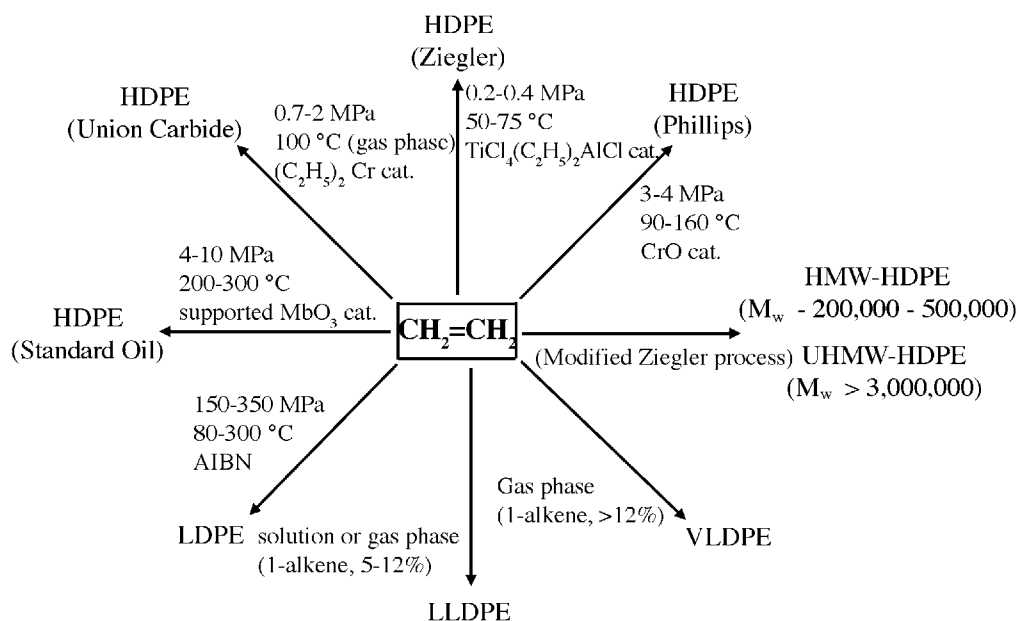


Figure 1.1 Different preparative routes for commercial PE [3]. M_w : molecular weight, AIBN: azo iso butyronitrile

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properties of the polymer can be controlled by adding specific amounts of reactants to the reactor. Impact strength, notched impact strength, and environmental stress cracking resistance all improve on increasing the molecular weight, but this is accompanied by a reduction in the ease of processing.

Table 1.2 gives information on various industrial processes of ethylene polymerisation.

Processors of food, speciality packaging, and custom films are better served by solution-polymerised linear low-density PE (LLDPE) in most cases. Solution technology provides ‘more homogeneous resins’, because polymer molecules form more uniformly than for other polymerisation processes. The key strength of solution technology is the ability to incorporate higher alpha-olefin comonomers (octene); gas-phase processes are limited to using hexene. LLDPE from higher alpha-olefins yields good stretch and toughness. Although gas-phase and solution processes can produce similar LLDPE film grades, a gas-phase produced resin tends to have more odour and taste than a solution-polymerised one. A solution-polymerised octene LLDPE resin, when compared with competing octane-modified and metallocene grades, has a lower melt flow index (MFI) at a similar density, and this MFI has advantages such as yielding higher sealing, haze and directional tear balance. For high-volume applications such as stretch films, gas-phase-produced resins can be as effective as solutions, the key advantages being processability and price. Up to 35% of Europe’s film makers often tend to blend lower-priced butene LLDPE with as little higher-priced high-pressure low-density PE (LDPE) as possible in order to be able to use LLDPE equipment. High-pressure LDPE, although higher priced than many types of gas-phase LLDPE, provides superior clarity, optimal neck-in, and draw-down performance. Blending LDPE with LLDPE to add melt strength and improve processability is still a useful technique, the use of which probably will not decrease in the future. Atofina introduced an ethylene–hexene copolymer that eliminates the need for blending for the production of shrink films. This material provides better rigidity than blends to allow downgauging and higher shrink speed for faster packaging rates, and easy tearing for faster and safer unloading of goods at retailers.

Table 1.2 Industrial processes of ethylene polymerisation [4]

Licensor	Process type	Product obtained and characteristics
Basell Technology Co. BV. A joint venture between Royal Dutch/Shell Group and BASF	Spherilene gas-phase technology; Ziegler–Natta titanium-based catalyst family; licensed capacity 1.8 MMT/y.	ULDPE (<900 kg/m ³) to HDPE (>960 kg/m ³); MFI ranges from 0.01 to 100 g/10 min; bimodal reactor grades, terpolymers.
Basell Polyolefins, Krupp UHDPE GmbH	Hostalen have diluent process, slurry polymerisation, stirred tank, two reactors in parallel or series, cascade technology Ziegler catalysts, 23 reaction lines, 2.9 MMT/y.	Unimodal and bimodal grades, MFI of 0.01 to over 50 g/10 min; for blow moulding (large containers, small bottles), extrusion moulding (film, pipes, tapes and monofilaments, functional packaging), injection moulding (crates, refuse bins, transport containers, fibres).
Borealis A/S	Borstar polyethylene process, loop and gas-phase low-pressure reactors in series, one cycle; Ziegler–Natta and single-site catalysts. Maximum design size for one line is 300,000 tonnes/y.	Bimodal and unimodal LLDPE, MDPE, HDPE, with full control of comonomer distribution; densities ranging from 918 to 970 kg/m ³ and MFI of 0.1 to over 100 g/10 min; for tailor-made applications for pipe strength, film bubble stability, high environmental stress crack resistance, and stiffness in blow moulding, extrusion coating, and wire and cables. PE80 and PE100 for pipes.
BP	Innovene gas-phase process, Ziegler–Natta, chromium, and metallocene catalysts. Chromium catalysts give broad molecular weight distribution (MWD) products and supported Ziegler–Natta catalysts produce NMWD products, while metallocene catalysts provide exceptional strength and clarity and easy processing; 30 reactor lines operations, capacity 50,000–350,000 tonnes/y.	LLDPE with either butene or hexene comonomers; used in film, injection moulding, rotational moulding, and extrusion applications. HDPE with NMWD provides superior injection moulding grades; broad MWD HDPE is used for blow moulding, pipe, film, and other extrusion applications.
Chevron Phillips Chemical Co., LP	LPE process from Phillips Petroleum Co., isobutane slurry, loop reactor, very high activity proprietary catalysts; comonomers: butene-1; hexene-1, 1,4 methyl-1 pentene, and octene-1, no waxes and other by-products, minimum environmental emissions; 82 reactor lines, 34% of worldwide capacity; slurry-loop reactor.	LPE homo- and co-polymers (density: 920–970 kg/m ³) for films, blow moulding, injection moulding, rotomoulding, pipes, sheets and thermoforming, and wire and cables.
EniChem through Snamprogetti	EniChem process, high pressure, autoclave or tubular reactor.	LDPE (density: 918–935 kg/m ³), MFI = 0.1–400 g/10 min. EVA copolymer (3–40% VA content) for film, injection moulding, profiles, sheets, cable sheetings, crosslinking, and foaming.
Exxon Mobil Chemical Co.	High-pressure free radical process; tubular or stirred autoclave reactor. Total installed capacity 1.7 MMT/y.	LDPE (density: 912–935 kg/m ³) and EVA (up to 30 wt% VA).

Table 1.2 Continued...		
Licensors	Process type	Product obtained and characteristics
Mitsui Chemicals Inc.	CX process, low-pressure slurry process, total capacity 3.6 MMT/y.	HDPE to MDPE (density: 930–970 kg/m ³), MFI = 0.01 to >50 g/10 min; MWD from narrow to very large, controlled.
Stamicarbon BV	COMPACT solution process, single proprietary Ziegler–Natta type catalyst, comonomers: propylene, butene, octane, or combination. Ethylene conversion exceeds 95%, low residence time, total capacity 650 MMT/y.	PE of any density (density: 900–970 kg/m ³); MFI = 0.8–100 g/10 min; for film, injection moulding, pipes, rotomoulding, and extrusion applications; crosslinking.
Stamicarbon BV	CRT technology – high-pressure clean tubular reactor, nonfouling reactor, constant pressure and temperature profile, peroxides as initiators, low-cost production, short residence times. Total licensed capacity 1.8 MMT/y.	LDPE (density: 918–930 kg/m ³ ; MFI = 0.2–70 g/10 min) and EVA (10 wt% VA) copolymers; for injection moulding, sheets, flexible pipes, cable sheathings, blow moulding, crosslinking, and foam, etc.
Univation Technologies	Unipol process, low-pressure, gas-phase, fluidised bed reactor, proprietary solid and slurry catalysts, low investment and operating costs, low level of environmental pollution, potential fire and explosion hazard; 89 reaction lines with capacity ranging from 40,000 to 450,000 tonnes/y.	LLDPE to HDPE (density: 915–970 kg/m ³ ; MFI = 0.1–200 g/10 min); for film, blow moulding pipes, rotomoulding, and extrusion applications.
<i>EVA: ethylene–vinyl acetate</i> <i>LLDPE: linear low-density PE</i> <i>MFI: melt flow index</i> <i>NMWD: narrow molecular weight distribution</i> <i>CRT: Clean reactor technology</i>		<i>HDPE: high-density PE</i> <i>MDPE: medium-density PE</i> <i>MMT: million metric tonnes</i> <i>ULDPE: ultra low-density PE</i>

High-density PE (HDPE) made with a slurry-loop reactor, which uses a chromium catalyst, has good organoleptics and features medium to broad MWD to boost high shear processability during film extrusion. HDPE is now produced by catalytic polymerisation of ethylene in slurry (suspension), solution, or gas-phase reactors. The catalyst choice and/or the use of bimodal processes are used to modulate the quality of the output. The traditional Ziegler–Natta (ZN) and chromium catalysts have been joined by metallocene catalysts, which give improved properties. Bimodal processes, using twin slurry, gas-phase, or combinations of reactors, allow one to produce resins that can compete with those produced using metallocene catalysts. Basell has developed a single, multizone reactor, which can produce bimodal and multimodal PE using ZN or single-site catalysts. DuPont has obtained a licence to use iron and cobalt tridentate catalysts. Dow uses UNIPOL technology as well as ZN and chromium catalysts.

The selection of catalysts and initiators is critical for the good running of the processes. Dow, Exxon Mobil, and Nova Chemicals have developed resins using single-site catalysts (SSC) that improve product performance by allowing one to tailor the MWD.

1.2 Strengths

PE is used more than any other thermoplastic polymer. There is a wide variety of grades and formulations available that have an equally wide range of properties. In general, the outstanding characteristics of PE are toughness, ease of processing, chemical resistance, abrasion resistance, electrical properties, impact resistance, low coefficient of friction, and near-zero moisture absorption.

This material evolved into two forms, LDPE and HDPE. PE's dominance can be explained by the fact that it offers a combination of characteristics that are ideally suited to various applications, such as good flow, good thermal stability, broad density range, and excellent chemical resistance.

1.3 Material Density/Percentage Crystallinity

Traditionally, PE has tended to be classed as low, medium, or high density. These sub-divisions have never been precisely defined. High-pressure polymerisation of ethylene takes place by a free radical process, medium-pressure polymerisation occurs in the presence of molybdenum oxide or chromium oxide (Phillips process), while for low- and medium-pressure polymerisation transition metal halide and alkylaluminium compounds (Ziegler process) are used. Some properties of PE obtained from various ethylene processes are presented in **Figure 1.2**.

Long-chain branching in polymers has a strong influence on MWD and hence on polymer properties, particularly rheological and film properties such as haze and gloss.

PE is cheap, flexible, durable, and chemically resistant. LDPE is used to make films and packaging materials, including plastic bags, while HDPE is used more often to make containers and plumbing and automotive fittings. HDPE's higher stiffness compared with LDPE and LLDPE allows film manufacturers to use it as a substitute to reduce thickness while keeping film properties constant.

Extrusion coating of paper and paperboard, the second-largest application segment, continues to be a growth area for LDPE, largely because of innovations in packaging technology for paperboard coating and paper and foil composite structures. The segment is growing at 1.5% presently, down from 3% five years ago. LDPE is easier to process than LLDPE and has good strength and clarity. The adhesives and sealants sector is also exhibiting positive growth at 1%.

1.4 Weaknesses

LDPE's largest market segment, films, continues to decline because of the increasing use of LLDPE in many applications. The trend in food packaging films is towards high-performance film structures. These are less permeable barrier films, designed to increase shelf life. Non-food packaging requires stronger films that allow downgauging, saving material and reducing cost. The biggest competition

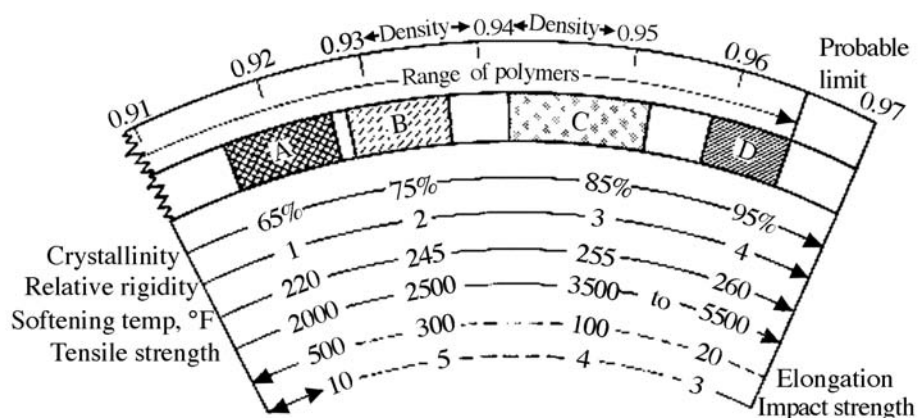


Figure 1.2 Range of properties obtained from various ethylene processes. A: typical high-pressure PE; B: copolymers; C: PE from the Ziegler process; D: PE from the Phillips process [5]

Redrawn from R.A.V. Raff in Encyclopedia of Polymer Science and Technology, published by Interscience, 1967. Copyright Wiley, 1967.

with LLDPE, however, is mainly in non-packaging applications: take-away food bags, rubbish bin liners, construction films, and disposable liners. In one segment there is resistance to LLDPE penetration. This is the high-clarity market for LDPE, which includes bags, bakery film, and textile and paper overwrap. Overall film use is declining by 0.4% per year. With the exception of extrusion coatings and adhesives and sealants, LDPE's other application segments are declining by 2–3% annually, largely as a result of displacement by LLDPE.

1.5 Applications

The applications of plastics in general and of PE in particular are innumerable. The main applications of PE are summarised in **Figure 1.3** and **Table 1.3**.

The consumption of LDPE at the European level is 4.7 million tonnes, of which film accounts for 60%. Co-extruded film permits a reduction in film thickness for the same mechanical resistance.

LDPE is mainly used as film (59%), extrusion coating (17%), injection moulding (6%), wire and cable (4%), adhesives and sealants (4%), sheets (2%), blow moulding (1%), and miscellaneous, including pipe, conduit, and rotomoulding (7%). There are also increasing demands for PE use in the medical field (growing demand for sterile packaging), the automotive sector (HDPE automotive fuel tanks is a booming business), cosmetics (innovative packaging designs), liquid food packaging, and twin-sheet thermoformed HDPE pallets to replace wooden pallets. HDPE is also used in pipes for canalisation (17%), injection moulded products (20%), industrial containers, packaging, housewares, and so on.

1.6 Material Price

The price of different materials depends on the grade, the quantity purchased, the supplier, etc. The prices of different grades of PE are compared in **Table 1.4**. These prices should be taken for guidance only.

Supply for PE and polypropylene resins remains tight due to strong demand from resin converters.

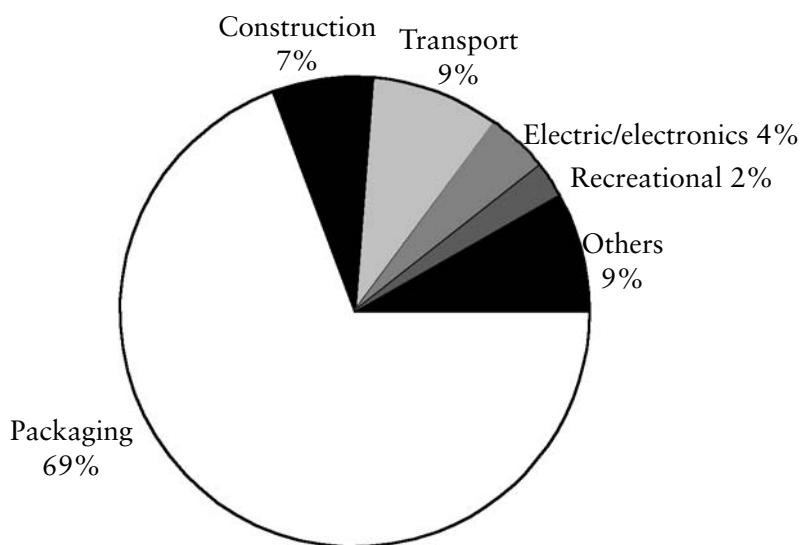


Figure 1.3 Main applications of PE [6]

*Redrawn from J.P. Forest, Revue Générale des Caoutchoucs et Plastiques, 2002, 78, 801, 42.
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Table 1.3 Main applications of PE	
Type of PE	Applications
HDPE	Pipe and pipe fittings for water, and petroleum tanks, toys, bowls, buckets, milk bottles, crates, containers, films for packaging, blown bottles for food, food cutting boards, corrosion-resistant wall coverings, pipe flanges, lavatory partitions, inspection covers in chemical plants, radiation shielding, self-supporting containers, prosthetic devices (implants), yarns, chemical drums, jerry cans, carboys, toys, picnic ware, household and kitchenware, cable insulation, carrier bags, food wrapping material.
LDPE	Chemically resistant fittings, chemical drums, tanks, and containers for storing water and most liquid fertilisers, pesticides, herbicides, insecticides, and fungicides, food storage containers, laboratory equipment, gas and water pipes, buckets, drinking glasses, insulation for wires and cables, core in UHF cables, disposable goods, gloves, kitchen tools, thermoformed products, corrosion-resistant work surfaces, vacuum formed end caps and tops, moisture barriers, liquid packaging, flexible and commercial packaging of photographic paper, extrusion coating grades, fittings and accessories, films or sheets for packaging, medical and hygiene shrink, shower curtains, unbreakable bottles, bowls, lids, gaskets, toys, packaging films, film liners, squeeze bottles, heat-seal films for metal laminates, squeeze bottles, toys, carrier bags, high-frequency electrical insulation, chemical tank linings, heavy duty sacks, general packaging.
LLDPE	Packaging, particularly film for bags and sheets. Lower thickness (gauge) may be used compared to LDPE. Cable covering, toys, lids, buckets and containers, pipes.
UHMWPE	Unit conveying: chain guides, star wheels, feed screws. Mining: truckbeds, hopper and bunker liners. Pulp and paper: suction box covers, rollers, foil blades. Medical: orthopaedic prostheses, knee, shoulder, and hip implants. Agricultural: food preparation surfaces. Automotive: lead–acid battery separators. Fibres: ballistic cloth, fishing lines and nets. Recreational: snow ski soles, snowmobile bogie wheels. Others: filtration material.
EVA material	Deep-freeze bags, agricultural film, shoe soles, teats, handle grips, flexible tubing, record turntable mats, beer tubing, vacuum cleaner hosing.
Chlorinated PE	Modifier for polyvinyl chloride (PVC) or compounded with LDPE or HDPE film to improve toughness; films are used as liners and for agricultural applications, flame retardant.
Wax emulsions, PE waxes (molecular weight ~ 2000)	Internal lubricants in PE (increase the melt flow index, do not increase the susceptibility to environmental stress cracking).
<i>UHF: Ultra high frequency</i>	

The present PE and polypropylene prices still do not allow for acceptable margins under the current market conditions. Based on this situation, Dow Plastics announced a price increase in Europe of €100 per metric tonne above January 2003 pricing levels for all polypropylene resins, Inspire performance polymers, LDPE resins and HDPE resins, Dowlex LLDPE resins, Attane ULDPE copolymers, Elite enhanced PE resins, and Aspun fibre grade resins.

Table 1.4 Indicative prices of different types of PE

Resin/grade	Volume category	
	I (US cents/kg)	II (US cents/kg)
High-density PE		
Blow moulding copolymer (HIC)	119-123	128-132
Blow moulding homopolymer (dairy)	119-121	123-130
Drums	125-130	132-139
Extrusion film HMW	132-136	141-147
Extrusion film MMW	132-134	139-147
Extrusion pipe HMW	143-147	154-161
Extrusion pipe MMW	150-156	158-163
Extrusion sheet	116-121	125-130
Injection GP	112-114	119-123
Rotomoulding powder	–	145-151
Low-density PE		
Extrusion 2,4-ethylene–vinyl acetate film	145-150	151-158
Extrusion clarity film	130-134	136-143
Extrusion coating paper	145-150	-
Extrusion film liner	134-139	141-151
Extrusion fractional melt	130-134	143-147
Injection GP	–	150-154
Injection lid resin	145-151	154-158
Linear low-density PE		
Butene-1 comonomer extrusion liner film	112-119	121-125
Butene-1 comonomer injection GP	–	114-123
HAO comonomer extrusion fractional melt film	130-136	139-145
HAO comonomer extrusion liner film	125-130	134-141
HAO comonomer injection GP	–	128-132
HAO comonomer lid resin	139-145	151-158
HAO comonomer rotomoulding powder	–	169-180
<i>I: annual volumes greater than 9 million kg</i> <i>II: annual volumes of about 0.9 million to 2.3 million kg</i> <i>GP: general purpose</i> <i>HAO: higher alpha-olefin</i> <i>HMW: high molecular weight</i> <i>MMW: medium molecular weight</i> <i>HIC: hydrogen-induced cracking</i> <i>Source data: Plastics News, 2003, 15, 37, 21</i>		

1.7 Market Share and Consumption Trends

For the year 2000, European consumption was 12 million metric tonnes (MMT). The Asia/Pacific region showed a consumption increase of over 1.2 MMT, while consumption in the developed regions increased by only 0.3 MMT. Global PE consumption increased by nearly 4%, or 1.9 MMT, to pass 50 MMT. While the LDPE market has been stagnating in North America and Europe, it has been growing in Asia, the Middle East, Africa, and Latin America. LLDPE has been and continues to be the fastest-growing member of the PE family. It recorded a healthy growth in consumption of about 8.5% in 2000. This growth is influenced, in part, by the demand for better packaging materials in the developed regions. In spite of a decrease in LDPE demand in the developed regions,

global consumption still managed to increase by nearly 1%. Substitution by LLDPE continues to be the primary reason for sluggish growth of LDPE. The sustained growth in consumption of HDPE is, in part, due to the increased use of the material in injection moulding applications, and it is replacing the use of PVC in pipe in the developed regions. HDPE is being used more frequently in fibre optic cable. The future outlook for PE consumption is positive, with global totals averaging approximately 5.7% growth over the next five years. According to Townsend, total PE consumption in 2005 will increase by over 16 MMT, reaching nearly 67 MMT. Consumption of LLDPE and HDPE will exceed overall PE growth averages while LDPE consumption is expected to grow by 2.7% annually. The consumption of polymers produced using metallocene catalysts continues to grow at a robust pace. The consumption of mLLDPE will grow at a much higher rate than that of LLDPE at 25% per year. In many developed countries mLLDPE is replacing conventional LDPE because of the higher performance of the former, which allows downgauging. Half of the volume increase (from 2001 to 2006) will be due to mLLDPE. In 2006 the consumption of mLLDPE should total around 4.2 MMT out of the 19 MMT overall LLDPE demand.

It can be noted that for LDPE the capacity surpasses the consumption, while for HDPE the situation is the opposite (Table 1.5). European demand for LDPE is around 5 MMT per year and has grown by an average of 1% per year over the past 10 years. Film and sheet applications account for 73% of total consumption and in blends with LLDPE. LLDPE demand is growing more rapidly at about 8% per year, and it is predicted to become the dominant polymer in Europe and North America. The trends in PE capacity and demand until 2012 are shown in Figure 1.4.

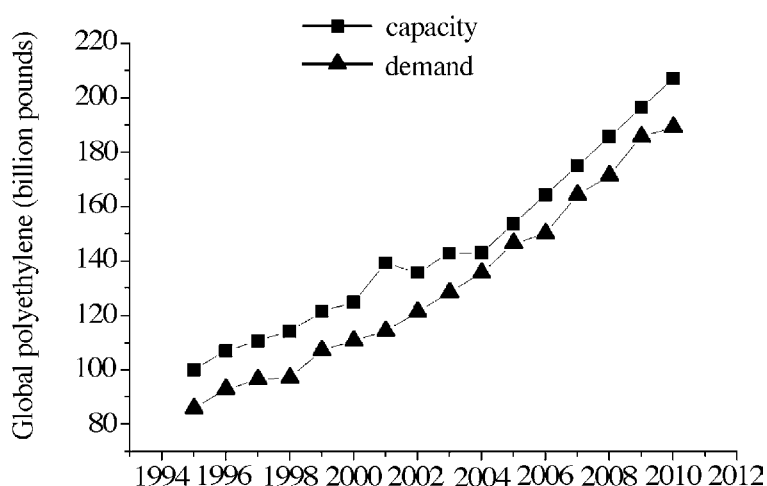


Figure 1.4 Global PE supply and demand forecast

Redrawn from DeWitt & Co. Inc.

PE type	1990		2001		2005	
	Capacity	Consumption	Capacity	Consumption	Capacity	Consumption
Low density	16.2	13.7	20.3	16.5	21.4	17.0
Linear low density	7.1	5.1	26.8	11.9	29.8	14.9
High density	11.2	11.8	20.1	21.1	21.5	24.8
Total PE	34.5	30.4	67.2	49.5	72.7	56.7

PE produced using metallocene catalysts (mPE) has captured nearly 7% of the world total LLDPE market. Consumption is expected to increase further at more than 25% annually over the next five years [7]. Global consumption of mPE resins has been virtually doubling every year since their commercialisation in 1995. With world consumption now estimated at close to 1 MMT, initial high growth rates are now slowing. By 2005 the world consumption will more than triple to 3.1 MMT. North America is presently the leading consuming region with nearly 42% of global consumption. The non-food packaging film markets consume the largest amount of mPE. However, food packaging film markets are projected to grow at the highest rate. In addition, stretch wrap and food lamination films are the largest mPE-consuming applications now and will remain so in 2005. Currently only two mPE producers, both in Japan, have dedicated metallocene capacity. All other mPE producers use their lines with metallocene capability to manufacture both mPE and conventional PE. As a result, current mPE capacity far exceeds production.

1.8 Major Suppliers

Major suppliers and their products and production capacity and market are presented in Table 1.6 and Figure 1.5, respectively. Exxon Mobil Chemical is a leading global PE producer and supplier.

Asia is the largest PE market at 14 billion kg consumed in 2001. North America is the second largest, consuming 12.7 billion kg, and Western Europe is the third largest market at 12.3 billion kg. North America PE exports are anticipated to shrink through 2005. The Asia Pacific region will increase its import demand, thus nearly doubling PE imports from 2000 to 2005. This demand will be primarily supplied from new capacity built in the Middle East.

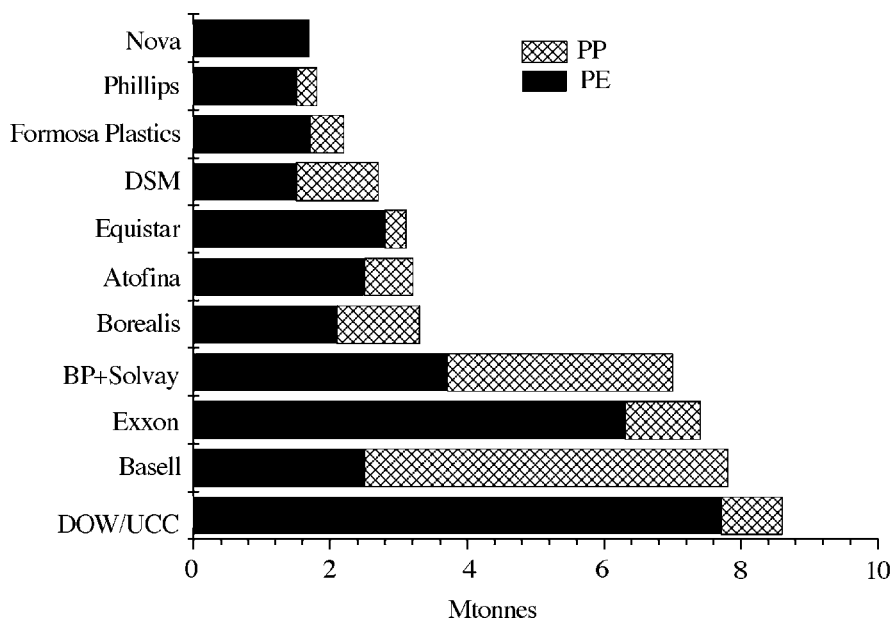


Figure 1.5 Production capacity of manufacturers of polyolefins at a worldwide level [6]
 Redrawn from J.P. Forest, *Revue Générale des Caoutchoucs et Plastiques*, 2002, 78, 801, 42.
 Copyright Societe D'expansion Technique et Economique, Paris, France, 2002.

Table 1.6 Major suppliers of PE

Supplier/process	Trade name, type of PE produced
AEI Compounds	Sioplas (crosslinked PE).
Albis	HDPE; LDPE.
Allied Signal	Paxon (HDPE and UV-stabilised, MDPE).
Arco Chemicals	Super Dylan.
Asahi Kasei KK, suspension	Metallocene-based HDPE.
Aspell Polymers	HDPE.
Atofina Petrochemicals, USA	HDPE.
Atofina UK Ltd (<i>locations for HDPE production: Antwerp, Feluy (Belgium), Gonfreville (France), locations for LLDPE production: Gonfreville (France)</i>)	MDPE, LLDPE.
Atofina	Finacene BM 359SG, Finathene B 593 MDPE and bimodal grades with hexene monomers.
Bamberger Polymers	Bapolene PE.
Basell (<i>locations for HDPE production: Frankfurt, Knapack, Münchmunster, Wesseling (Germany), Taragona (Spain), locations for LLDPE production: Wesseling (Germany)</i>)	HDPE, LLDPE.
BASF, gas phase	Lupolen 5021 D or D/BLA, Lupolen 1800 H, Lupolen 1800 LD (LDPE), Lupolen 1842 LD (LDPE) Lupolen 5021 HD (HDPE and UV-stabilised), Lupolen V (EVA, 12% VA), Neoplen 1710 (crosslinked PE), Neoplen 6132 (PE foam).
Borealis Chemicals/Borstar, suspension, gas phase (<i>locations for HDPE production: Schwechat (Austria), Beringen (Belgium), Porvoo (Finland), Burghausen (Germany), Ronningen (Norway), Stenungsund (Sweden), Sines (Portugal), locations for LLDPE production: Porvoo (Finland), Stenungsund (Sweden)</i>)	Statoil HDPE and UV-stabilised, Stanoil LDPE, Borocene, Neste LDPE, Neste LLDPE, Statoil LDPE, Borstar HF 6081 (bimodal HDPE), Optene (EVA copolymer, 12–33% EVA).
BP Chemicals Ltd; Dow/Innovene gas phase (<i>locations for HDPE production: Lavera (France), Grangemouth (UK), locations for LLDPE production: Grangemouth (UK)</i>)	Rigidex, Novex (LDPE), Eltex Tux 100 PE for corrosive pipe applications, thin walls for 16% weight saving.
BP Solvay Polyethylene	HDPE.
BP Chemicals	Novex (LDPE and UV-stabilised), Rigidex (HDPE, MDPE, and UV-stabilised).
BSL (<i>location for HDPE and LLDPE production: Schkopau (Germany)</i>)	HDPE, LLDPE.
Chevron Chemical Company or Chevron Phillips Chemical	Gulf PE (LDPE and UV-stabilised), HiD (HDPE, MDPE, and UV-stabilised).
CIPEN (<i>locations for LLDPE production: ND de Gravenchon (France)</i>)	LLDPE.
Cornelius Group PLC	
Daelim (Korea)	HDPE.
Deliway Ltd	
Dex Plastomers (<i>location for HDPE and LLDPE production: Beek (Netherlands)</i>)	LLDPE, HDPE.

Table 1.6 Continued ...	
Supplier/process	Trade name, type of PE produced
Dow Chemical Co. Ltd/Dowlex, solution (<i>locations for HDPE production</i> : Tessenderlo (Belgium), Terneuzen (Netherlands), Tarragona (Spain), <i>locations for LLDPE production</i> : Tarragona (Spain), Terneuzen (Netherlands))	Affinity polyolefin plastomers. Attane ULDPE. Dow HDPE, Dow LDPE, Dow MDPE, Dow LLDPE, Dowlex, Flexomer (VLDPE), Primacor copolymers, Tuflin LLDPE, Unival HDPE, Elite EPE, Dow butene LLDPE, Dow CPE, Tyin CPE (chlorinated PE).
DSM/Compact, solution (<i>locations for HDPE production</i> : Gelsenkirchen (Germany), Beek (Netherlands), <i>location for LLDPE production</i> : Gelsenkirchen (Germany))	Stamylan HD (HDPE), Stamylan MD (MDPE), Stamylan LD (LDPE and UV-stabilised); Stamylan UH (UHMWPE), Stamylex PE (for LLDPE), Stamylex XL (crosslinked PE).
DuPont	Alathon; Sclair (LLDPE), Siclairlink (crosslinked PE), Elvax (EVA copolymers, 12–33% VA).
Eastman Chemical Co.	Tenite PE (LDPE and UV-stabilised).
Elenac	
Elf Atochem	Lacqtene HD (HDPE and UV-stabilised); Lacqtene HX (LLDPE), Lacqtene CX (crosslinked PE) Lacqtene LX (LLDPE), Evatane (EVA copolymers, 12–33% EVA).
EniChem	Eraclene (HDPE); Riblene (LDPE and UV stabilised), Flexirene (LLDPE); MQF0 – ULDPE, Greenflex (EVA copolymers, 12–33% EVA).
Equistar/Maruzen/Nissan, suspension	
Erdolchemie (<i>location for LLDPE production</i> : Cologne (Germany))	LLDPE.
Evolve Japan	LLDPE.
Exxon Mobil Chemical	Escorene LDPE, Escorene LLDPE, Escorene EVA, Escorene ULTRA EVA (EVA copolymers, 12–33% EVA); Exceed 1012 CA (new metallocene-based VLDPE grade (912 kg/m ³) with exceptional toughness and strength and dart impact), Exact 4041 (ULDPE).
Federal Plastics	FPC PE (LDPE and UV-stabilised)
Formosa Plastics	
Franceschetti Elastomeri – Italy, Brescia	Marfan, Elifran, PE and thermoplastic elastomers.
Goodfellow	HDPE; LDPE.
Celanese Hoechst (Ticona)/Hostalen, suspension	Hostalen HD (HDPE and UV-stabilised), Hostapren (chlorinated PE), Hostalen GUR (for UHMWPE).
Hanwha Chemical (Korea)	LLDPE.
Huls	Vestolen A (HDPE and UV-stabilised).
Hyundai Petrochemical (Korea)	HDPE, LLDPE.
Idemitsu Petrochemicals	HDPE, LLDPE.
Indian Petrochemicals	
Ipiranga Petroquimica	
Japan Polychem	HDPE, LLDPE.
Japan Polyolefins	HDPE.

Table 1.6 Continued ...

Supplier/process	Trade name, type of PE produced
Lati	Latene EP (ethylene–propylene copolymers).
Mitsui Plastics	Hisek (LDPE and UV-stabilised).
Mobil Chemical	Mobil PE (LDPE and UV-stabilised).
Molekula Fine Chemicals	
Monmouth Plastic	Empee PE (HDPE, HDPE, UV-stabilised, MDPE).
Montell/Spherilene, gas phase	
Mitsui Plastics/Evolue, gas phase or suspension	Hisex.
Neste Chemicals UK Ltd	
Nippon PC, suspension	
Nova Chemical/Scclair, solution	Sinclair Astute FP (density = 0.920 g/cm ³); AST.
Pemex, Mexico	HDPE.
Petrofina	
Phillips Chemical, suspension	Marlex LLDPE.
Polymer	Ultra Wear (UHMWPE).
Polimeri Europa (<i>locations for HDPE production: Brindisi, Porto Torres, Priolo (Italy), locations for LLDPE production: Brindisi, Priolo (Italy), Dunkirk (France)</i>)	HDPE, LLDPE.
Reliance Industries	
Repsol Quimica (<i>locations for HDPE production: Puertollano, Tarragona (Spain)</i>)	HDPE, LLDPE.
Rexene Products	Rexene PE (LDPE and UV-stabilised).
Quantum Chemical	Petrothene (LDPE and UV-stabilised), Ultrathene EVA (EVA copolymers, 12–33% EVA).
Sabir	HDPE, LLDPE.
Shuman Plastics	Shuman PE (LDPE and UV-stabilised).
SK Corp. (Korea)	LLDPE.
Solvay Chemicals, suspension (<i>locations for HDPE production: Antwerp (Belgium), Sarralbe (France), Rosignano (Italy)</i>)	Eltex (HDPE).
Sentrachem	
Tripenta Ltd	
Thai Petrochemical Industries	
Tiszai Vegyi Kombinat	
Ube Industries	UBE PE (LDPE and UV-stabilised).
Union Carbide	
Univation/Unipol, gas phase	
Westlake	HDPE, LLDPE.
Zotefoams	Plastazote and Plastiroll (PE foam).

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2 Basic Types

Polyethylene (PE) grades are mainly classified according to their density (Figure 2.1).

2.1 Homopolymers and Olefin Copolymers

2.1.1 Low-Density Polyethylene (LDPE)

LDPE is a semi-rigid, translucent material, and was the first of the polyethylenes to be developed. It is primarily used at 'normal' operating temperatures. Its qualities include toughness, flexibility, resistance to chemicals and weather, and low water absorption. It is easily processed by most methods and has a low cost. It is also resistant to organic solvents at room temperature. Its use is not advisable in situations where extreme temperatures are found. It is a corrosion-resistant, low-density extruded material that provides low moisture permeability. LDPE has a fairly low working temperature, soft surface, and low tensile strength. It is an excellent material where corrosion resistance is an important factor, but stiffness, high temperature, and structural strength are not important considerations.

LDPE resins are re-emerging as a valuable product family, combining superior clarity with a stiffness and density favoured by converters for downgauging. Ease of processing beyond most linear low-density PE (LLDPE) resins, combined with improved product performance, continues to give cost-competitive solutions to converters in a wide variety of film applications. These range from complex food packaging structures to shopping bags, coated paperboards, liners, overwraps, consumer bags, heavy-duty sacks, clarity shrink and collation films, lamination films, agricultural films, extrusion coatings, caps and closures, and a variety of durable products such as power cables and toys. In packaging applications Dow LDPE resins offer excellent aesthetics, printability, strength, tear resistance, and elasticity. In cost-sensitive health and hygiene markets LDPE resins can improve processing efficiencies, and can be used for wire, cable, pipes, and other goods.

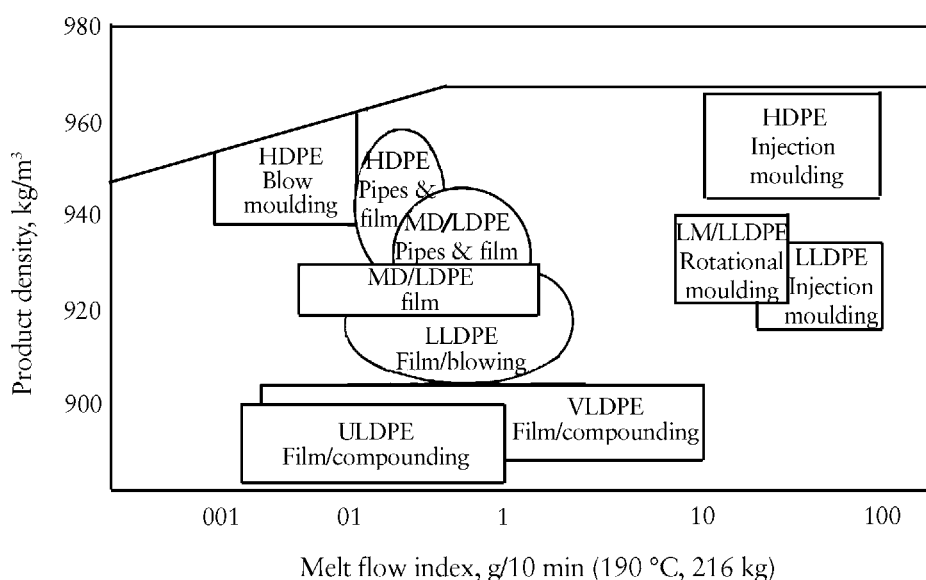


Figure 2.1 Classification of PE grades. HDPE: High-density PE, MDPE: Medium-density PE, LDPE: Low-density PE, LLDPE: Linear low-density PE, ULDPPE: Ultra low-density PE, VLDPE: Very low-density PE, LMDPE: low medium-density PE

Redrawn from Tecnon Orbichem. Copyright Tecnon Orbichem

LDPE is lightweight and formable, has a high impact resistance and excellent electrical properties, and is machinable and weldable. LDPE can be processed by all conventional methods: hot gas welded, fusion and butt welded, ultrasonically sealed, die cut, machined with wood- or metal-working tools, vacuum formed, and thermoformed. The long side-chain branching of the LDPE molecules produces a more amorphous polymer having a lower melting point and higher clarity compared to LLDPE. LDPE is also differentiated from LLDPE by poorer physical properties as regards tensile strength, puncture and tear resistance, and elongation. LDPE has very good flow behaviour and excellent resistance to chemicals. It is flexible and tough at low temperatures, transparent in thin films, and has very good environmental stress crack resistance (ESCR). UV-stabilised LDPE is used in agricultural/building components and sheeting film.

LLDPE resins are ideal for downgauged lids and a variety of parts such as industrial containers, rubbish bins, automotive parts, closures, and similar items. LLDPE resins exhibit high gloss and low odour and most are suitable for packaging applications under US Food and Drug Administration (FDA) regulations.

The disadvantages of LDPE are its low strength, stiffness, and maximum operating temperature, flammability, poor UV resistance, high gas permeability (particularly CO₂), and susceptibility to environmental stress cracking.

Today, it has almost totally been replaced by LLDPE. The main market for LDPE is in high-clarity products, which includes produce bags, bakery film, and textile and paper overwrap. Overall film use is declining by 0.4% per year. With the exception of extrusion coatings and adhesives and sealants, LDPE's other application segments are declining 2–3% annually, largely as a result of displacement by LLDPE.

2.1.2 High-Density Polyethylene (HDPE) Resins

HDPE resins provide toughness (temperature toughness to –60 °C), rigidity, and strength for blow-moulding applications, extruded and film products, and injection moulded items. They offer an excellent combination of stiffness and ESCR, and have many applications in personal care, household, industrial container, and bottle products.

HDPE resin is a flexible, translucent/waxy material. It is weatherproof, easy to process by most methods, has a low cost, and has good chemical resistance.

HDPE pipe resins offer the superior toughness and stress crack resistance essential for pipe extrusion, while high molecular weight HDPE (HMWHDPE) film resins provide toughness and downgauging capabilities for products such as thin-gauge carrier bags, bin liners, and refuse sacks.

HDPE resins offer both strength and processability – the two properties every injection moulding processor wants, but rarely obtains at the same time. This advantage is available across the wide spectrum of end-use applications. The range includes homopolymers and copolymers, with a variety of melt indices and densities. Dowlex improved processing resins bring to fabricators better flow characteristics compared to other HDPE with similar melt indices.

2.1.3 High-Density Polyethylene

HDPE is more rigid and harder than lower density materials with a molecular weight below 300,000 g/mol. It also has a high tensile strength, four times that of LDPE, and has high compressive strength. HDPE meets FDA requirements for direct food contact applications. It is also accepted by the US Department of Agriculture (USDA), National Science Foundation (NSF), and the Canadian Department of Agriculture.

The extremely high molecular weight of HDPE combined with its very low coefficient of friction produces an excellent abrasion-resistant product which is resistant to gouging, scuffing, and scraping.

HDPE has exceptional impact strength, being one of the best impact-resistant thermoplastics available, and has excellent machinability and self-lubricating characteristics. Its properties are maintained even at extremely low temperatures. HDPE has stress cracking resistance and very good chemical resistance to corrosives (with the exception of strong oxidising acids at elevated temperatures). Certain hydrocarbons cause only a light surface swelling at moderate temperature. Moisture and water (including saltwater) have no affect on HDPE. It can be used in freshwater and saltwater immersion applications. HDPE can be hot gas welded, fusion and butt welded, ultrasonically sealed, die cut, machined with wood- or metalworking tools, vacuum formed, and thermoformed.

Representing the largest portion of PE applications, HDPE offers excellent impact resistance, is of low weight, has low moisture absorption, and has high tensile strength. HDPE is stronger and stiffer than LDPE but its impact strength is not as good at low temperatures. It is also more prone to warpage due to its higher crystallinity, which makes it very sensitive to differential cooling rates across the walls of rotomoulded products. HDPE also has higher shrinkage than LDPE. HDPE is also non-toxic and non-staining and meets FDA and USDA certification for food processing. Borstar HF 6081 (bimodal HDPE) is designed for jacketing all self-supporting dielectrics, and for optical cables, which provide high optical-fibre counts, toughness, and weather and UV resistance, and can be used under severe installation and in-service conditions.

Unival HDPE resins have been developed for blow-moulded bottles, drums, and other industrial containers. These resins have excellent rigidity, superior stress crack resistance, high impact and melt strength, and moderate swell. Unival resins are used to produce bottles up to 20 gallons in size used to contain household industrial chemicals, toiletries and cosmetics, health and medicinal aids, food products, and milk, juice, and water.

Blow-moulding applications such as bottles, packaging containers, car fuel tanks, toys, and household goods account for over 27% of world demand. Film and sheet uses include wrapping, refuse sacks, carrier bags, and industrial liners. Injection-moulding grades are used in crates, pallets, packaging containers, housewares, and toys. Extrusion grades are typically used in pipes, wire coating, and cable insulation.

HDPE does have certain disadvantages. It is susceptible to stress cracking, has lower stiffness compared to polypropylene (PP), high mould shrinkage, and poor UV resistance. It is also available in a UV-stabilised form that has better UV resistance, but the tensile strength and elongation at break are reduced compared with unmodified HDPE. HDPE may give off dangerous fumes if strongly heated, and dense smoke is formed when it burns. Dust can be an irritant to the eyes, skin, and respiratory system.

2.1.4 Medium-Density Polyethylene (MDPE)

MDPE is normally a mixture of LDPE and HDPE and therefore has a property profile somewhere between these two materials. As with the other grades, its role has decreased significantly with the introduction of linear grades. It has good impact and drop resistance, is less notch sensitive and has a better cracking resistance than HDPE, but its hardness and rigidity is less compared to HDPE. It is used for gas pipes and fittings, sacks, shrink film, packaging film, carrier bags, and screw closures.

The most common use of MDPE is as a facing component in combination with HDPE, LDPE, LLDPE, or metallocene LLDPE. Blends of MDPE with HDPE are predominantly used in the traditional HDPE film applications mentioned above. When blended with LDPE or LLDPE, MDPE

is suitable for film applications such as shrink films, deep-freeze bags, and bags for heavy articles. The three-layer LDPE/MDPE/LDPE film laminate combines good optical and mechanical film properties with good sealing properties.

MDPE has an average molecular weight of between 200 and 300 kg/mol and a broad molecular weight distribution (MWD). MDPE film raw materials have a high load melt flow rate (HLMFR) of between 10 and 25 g/10 min.

2.1.5 Linear Polyethylenes

The lower density of LDPE relative to HDPE is caused by the fact that molecules of LDPE have many more relatively long branches off the main molecular chain. This prevents the molecules from packing as closely together as they do in HDPE. Linear PE materials have more side branches than LDPE but they are comparatively short. This has the advantage of improving the strength and stiffness of these materials relative to LDPE, as well as the puncture and the anti-tear properties, while retaining the excellent low-temperature toughness of LDPE. LLDPE is manufactured through a variety of processes: gas phase, solution, slurry, or high-pressure conversion. Linear PE have proved to be particularly well suited to rotomoulding. LLDPE is widely used for all types of tanks, drums, containers, hoppers, bins, etc. It is possible to produce all densities using the linear process. Sinclair Astute FP grades are easily processed into multilayer film for food and speciality packaging, laminations, and heavy-duty shipping sacks. They have a density of 0.920 g/cm³ and a melt flow index of 1.0 g/10 min. They have a good dart impact, puncture resistance, sealing performance, optical properties, and tear strength.

Dow butene LLDPE resins, produced via the solution process, offer the lowest cost for less demanding films. They are characterised by excellent optics, processability, and sealing performance, better bubble stability because of a higher melt strength, better haze, and better gloss. Applications include general-purpose packaging, industrial packaging, food and speciality packaging, stretch cling film, and agricultural films.

Most LLDPE are now produced with butene-1 as comonomer. However, there is a new trend towards the increased use of higher alpha-olefins (4-methylpentene-1, hexane, or octene) during the polymerisation of ethylene to give a resin with a similar density to LDPE, but the linearity of HDPE. Solution, slurry, or gas-phase processes are used, and many processes vary between LLDPE and HDPE production, although many plants tend to be dedicated to one or the other. The main application of LLDPE in Western Europe is for blending with LDPE for film production. The normally used proportions of LLDPE (20–25 wt%) improve the draw-down, puncture resistance, and heat sealing properties, whereas the processing properties of the mixtures largely correspond to those of LDPE.

Tuflin LLDPE resins, branded the ‘workhorse’ of hexene materials, are used in numerous film applications including stretch, food packaging, and industrial films. Films extruded from Tuflin resins exhibit superb toughness, high tensile strength and elongation, excellent tear and puncture resistance, high stiffness, and are readily heat-sealable. Tuflin resins are low-melt-index resins that can be slip, antiblock, and antioxidant modified. Tuflin resins are recommended for making high-quality packaging films, including stretch and cling wraps, as well as for the manufacture of films in a wide range of gauges – from less than 25 µm to greater than 125 µm. Tuflin resins can be used as blending resins to upgrade the film properties of other PE resins that have much lower toughness.

World growth of LLDPE is forecast between 6 and 9% per year to 2005, and LLDPE will continue to make inroads into traditional LDPE markets. Several new plants are being planned in the Middle East, where LLDPE capacity will double between 2000 and 2005, with a resultant significant increase in exports to European and Asian markets.

LLDPE should not be exposed to flames, as it gives off dense smoke on burning. Flammable mixtures can be formed in air during a fire.

2.1.6 Very Low-Density Polyethylene (VLDPE) Resins

These are extremely flexible olefin copolymers that deliver additional flexibility to blown film, enabling converters to run thinner single-layer, multilayer, or thick films, on existing lines, at faster output rates. Flexomer resins bridge the gap between plastics and rubbers, and provide excellent strength, toughness, and flexibility over a wide range of temperatures and, when blended or coextruded with other polymers, deliver improved toughness, tear, dart impact, and puncture resistance. They are used for hose and tubing, ice and frozen food bags, food packaging, and stretch wrap, as well as impact modifiers when blended with other polymers. Flexomer resins for alloys and blends provide superior performance differentiation and compounding versatility, helping formulators expand existing product lines to include a range of new compounds. When used with traditional polyolefins (PO), Flexomer resins from Dow deliver added protection, improved elasticity, good impact resistance, and stress dispersion – all at a competitive price.

2.1.7 Ultra Low-Density Polyethylene (ULDPE) Resins

Dowlex PE resins and Attane ULDPE resins help converters meet demanding performance requirements in very specific market segments, such as stretch wrap, food packaging, health, and hygiene. Attane ULDPE resins offer greater low-temperature flexibility and flex crack resistance, ideal for containing liquids that move freely within a package. Leaks and spills are avoided, and the package still offers excellent optical properties, high tear resistance, and other key properties for customers. Packaging applications include heavy-duty sacks, turf bags, consumer bags, and packaging for cheese, meat, coffee, and detergents. Other applications include silage wrap, mulch films, extruded membranes, heating and water pipes, and injection moulded products.

Some of the characteristics of the different PE types discussed previously are presented in **Table 2.1**. The type of chains and the degree of branching determine the ultimate properties of a polymer. The properties can be tailored by adjusting the polymerisation method or the reaction conditions to favour differing degrees and forms of branching along the backbone.

PE	Density (g/cm ³)	Number of branches (per 1000 carbon atoms)	Degree of crystallinity (%)	Comments
LDPE	0.910–0.925	20–30 (methyl); 3–5 (<i>n</i> -butyl)	40–50	<i>n</i> -Butyl branches arise from backbiting
VLDPE	0.890–0.915	Numerous	–	–
LLDPE	0.910–0.925	–	–	Only contains short branches
HDPE	0.942–0.965	<4 (Phillips); 5–7 (Ziegler)	60–80	No ethyl or butyl (Phillips); ethyl branches (Ziegler)
MDPE	0.926–0.940	4–6	–	Formed from blending LDPE/HDPE or LLDPE copolymer

2.1.8 Metallocene Polyethylene (mPE)

Metallocene PE is made with a metallocene catalyst or single-site catalyst (SSC) in a slurry loop process. These grades are copolymer materials with very narrow MWD, specifically formulated for rotational moulding. These materials have superior mechanical properties, a significantly reduced low molecular weight (i.e., extractable) content, and even better whiteness than the traditional LLDPE materials. Metallocene grades now account for about 15% of global LLDPE consumption

and market penetration is expected to reach 20% in five years. Exxon Mobil introduced a very low-density mPE in North America in 2001, becoming the first licensee of the technology from Univation. Dart impact is three times better than conventional VLDPE and the sealing temperature is only 85 °C. It is expected that mHDPE consumption will grow by 30% per year up to 2006. The material is a target for food and industrial applications because of its toughness and strength. Bimodal grades exhibit improved tear strength and processability. Metallocene catalysts have not yet as much impact in the production of HDPE.

2.1.9 Bimodal Grades

Bimodal grades, offering low weight and higher strength, have high- and low-molecular weight components in similar concentration, having a broader processing range than conventional materials. Bimodal material technology has been available for over a decade, but it was not pursued much until recently because expensive multi-reactor technology was required to synthesise the low- and high-molecular weight components. Recent catalyst and reactor technology developments enable bimodal-grade production with improved economics. They are designed mainly for blow-moulded containers (bottles). They have higher die swell and ESCR. The ESCR of the bimodal grade is above 100 hours, three times that of some unimodal grades. The combination of higher melt strength can limit sagging of bottle parisons, improving material distribution and reducing waste. Processors can reduce container weight by as much as 15% while maintaining stiffness and also can increase the amount of post-consumer recycle in each bottle by up to 25%, thereby reducing costs with virtually no property loss. These grades also offer advantages in pipe manufacture because of the possibility of thinner pipe walls with the same operating pressure. New generations of bimodal PE80 and PE100 are designed for drinking water and gas applications because of their high strength and good long-term properties. Recent years have seen increasing interest in bimodal/multimodal HDPE, which provide outstanding properties, both intrinsically in the material and in the finished parts. These intrinsic 'polymer alloys' or 'reactor blends' combine high stiffness with unprecedented toughness. The crack resistance (e.g., in pipes) is several orders of magnitude higher than that of unimodal materials. Bimodal/multimodal HDPE products are polymerised in cascade processes, e.g., with series-connected reactors, each of which performs a specific sub-process.

2.1.10 UV-Stabilised Grades

These have better resistance to UV degradation than unmodified grades, although they are slightly more expensive. Tensile strength and elongation at break are reduced. They are applicable for rotationally moulded storage tanks and vessels, milk bottle crates, agricultural/building components, and sheeting film.

2.1.11 Crosslinked Polyethylene (XPE)

XPE is unique in the PE family in that the molecular chains in the final product are linked together in a three-dimensional network. The crosslinking of the molecular chains can occur during the moulding operation, or the necessary chemical reaction can be activated in the solid product after moulding. Crosslinking imparts high strength, toughness (even at low temperatures), and excellent stress crack resistance. These properties make it ideal for high-performance containers, such as tanks for aggressive chemicals. Compared with other PO (such as PP), XPE is characterised by better thermal stability, time-to-failure at 95 °C, stress crack resistance, flexibility, impact strength, tolerances, tensile strength, and creep behaviour. XPE is more durable under temperature extremes and chemical attack, and resists creep deformation, making it an excellent material for hot water applications (up to 93 °C). Crosslinked LDPE is still the general insulating material for power cables in the voltage range above 10 kV. In the 1 kV range, however, silane-cured LLDPE is predominant.

XPE pipes, almost entirely limited to heating and sanitary applications in the past, are now gaining importance as supply lines for gas and drinking water, for example in Germany. XPE pipes are used where the specific advantages of XPE, such as notch insensitivity and outstanding resistance to rapid crack propagation, can be exploited. Examples include pipes for bedless or trenchless laying in sand and house connection lines. A further application of XPE pipes is as district heating lines, service temperatures up to 95 °C not being a problem because of the excellent heat resistance. XPE tubing is not intended for outdoor applications and must be stored in a covered environment not exposed to direct sunlight. Maximum UV exposure is no more than 60 days.

2.1.12 Ultra High Molecular Weight Polyethylene (UHMWPE)

UHMWPE is a linear homopolymer produced by the polymerisation of ethylene gas in the presence of a highly reactive organotitanate catalyst. UHMWPE was first synthesised by Karl Ziegler in the early 1950s and introduced commercially in 1955. Structurally, it is similar to HDPE, differing in the average length of its chains. The average molecular weight is 10–100 times greater than standard grades of HDPE (higher than 3.1×10^6 g/mol). Commercial grades have molecular weights of $3\text{--}6 \times 10^6$ g/mol. UHMWPE is of low weight (one-eighth the weight of mild steel), high in tensile strength, and as easy to machine as wood. It exhibits the best sliding wear resistance and impact toughness of any polymer, routinely replacing steel. Figures 2.2 and 2.3 compare the impact resistance and abrasion resistance of UHMWPE with other competing materials.

UHMWPE is the ideal material for many parts subject to wear in machinery and equipment as well as a superb lining in material handling systems and storage containers. It is self-lubricating and resistant to shattering, wear, abrasion, and corrosion. It meets FDA and USDA standards for food and pharmaceutical equipment and shows good performance in applications up to 82 °C or when subjected to periodic cleaning with steam or boiling water for sterilisation [2].

2.1.13 Ultra High-Modulus Polyethylene

In order to produce an oriented PE whose Young's modulus at low temperatures approaches the theoretical value of the crystal chain modulus (about 300 GPa), several production methods can be used. These include spinning techniques and a two-stage draw process in which an initial stage of drawing (draw ratio $\times 8$) is followed by a continuing stage of extension, so that the already drawn material thins down to achieve a final draw ratio of $\times 30$ or more.

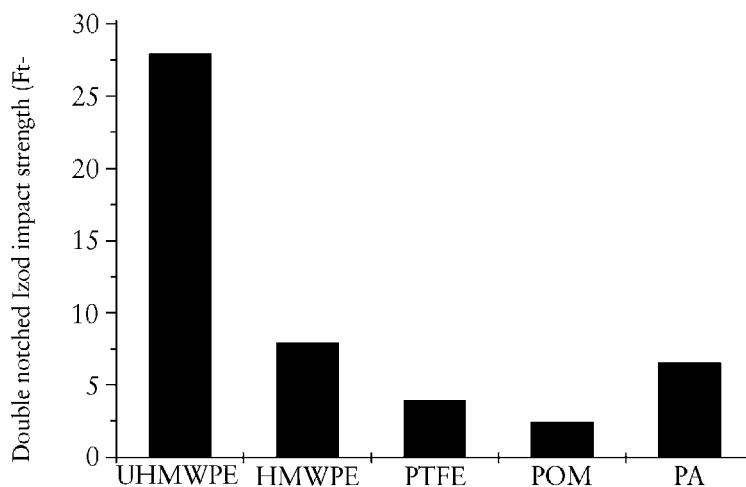


Figure 2.2 Comparative Izod impact strength for various polymer types (PTFE: polytetrafluoroethylene, POM: polyoxymethylene, PA: polyamide)

Source: <http://k-mac-plastics.com/primeresins/uhmwpe-virgin-plastic-for-sale.htm>.

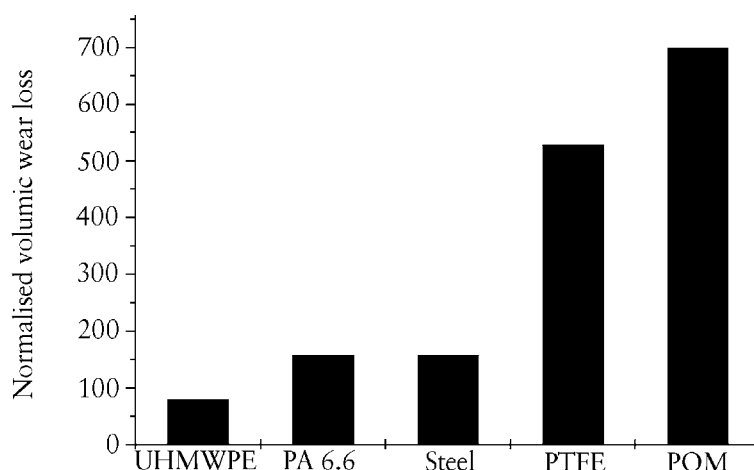


Figure 2.3 Comparative sand-slurry abrasive wear resistance for various materials (PA6.6: polyamide 6.6)

Source: <http://k-mac-plastics.com/primeresins/uhmwpe-virgin-plastic-for-sale.htm>.

2.1.14 Polyethylene Foam Resins

Types of PE foam include non-XPE, XPE, and expandable PE (EPE) beads [3].

During the production of XPE foam there are several options for crosslinking: peroxide, silane, or irradiation. XPE foam, representing approximately 24% of all PE foams, is expected to grow by 6.6% compared to 3.8% for non-XPE foam. The PE foam market is divided into a variety of segments, the main ones being packaging, sporting goods/recreational, automotive, and profiles. The protective packaging segment accounts for 54% of the market, followed by sporting goods/recreational at 13%, profiles at 12%, and automotive at 11% (Figure 2.4).

PE foams exhibit a superior ability to absorb mechanical impact, reduced hygroscopicity, low permeability to water vapours, and good resistance to weathering and chemicals compared to polystyrene (PS) and polyurethane (PU) foams. They are rigid or flexible foams depending on the volume increase which may be anything from three to five to as much as 40 times the initial volume.

The SSC resins, combined with foam producers' crosslinking technology, have allowed foam producers to penetrate market segments (such as automotive) that require softer foams. The packaging segment constitutes more than half of the PE foam market. For transporting high-value items such as computers and electronic components: PU, PE, PS, and PP foams are used for protective packaging. In such cases the correct resin selection and product design is critical. Once the fragility level for a product is determined by experimental means, a foam material and its required thickness can be selected by using the appropriate cushioning curves for various foam products. An economical balance between material cost and cushioning functionality is also important.

In practice the ultimate growth potential for PE foam *versus* PS and PU foams is limited by the basic characteristics of PE. They have low glass transition temperatures (T_g) and the flexural modulus range is limited compared with PU foams. The introduction of SSC PE has increased the potential flexural modulus range.

PE foams have excellent barrier properties, are thermoformable, have excellent chemical resistance, and are available in fire-retarding forms; however, they are more expensive than PS

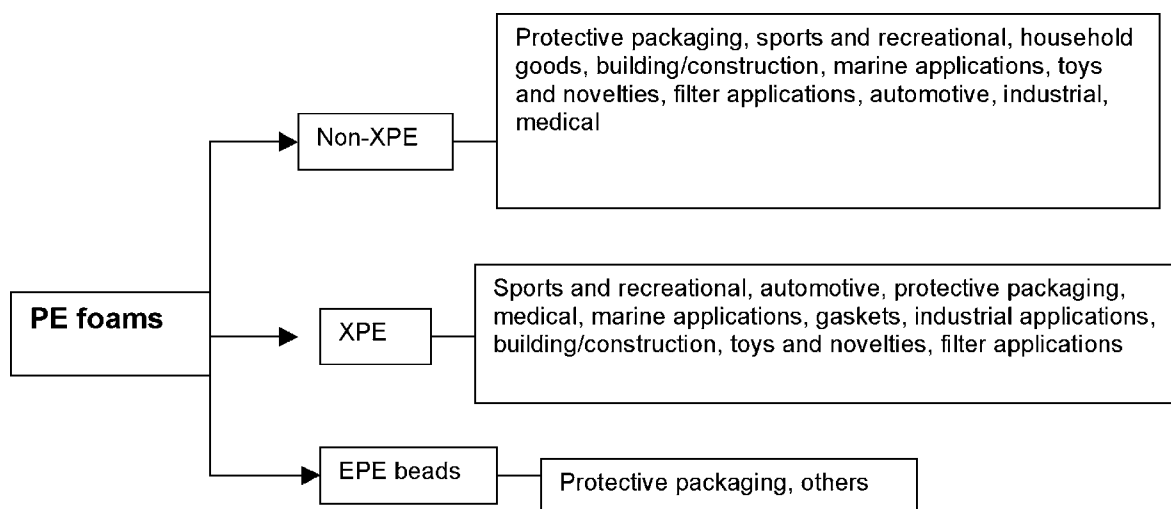


Figure 2.4 Main applications of PE foams

Source: Chemical Markets.

foams. Applications are in impact-sensitive equipment, replacement for tissue paper, water pipe insulation, and acoustic cladding. Trade names include Neopolen (BASF), Plastazote, and Plastiroll (Zotefoams).

LDPE resins have a broad MWD and long-chain branching that contribute to a high degree of shear thinning and good melt strength, and are the most widely used materials for foam processing. HDPE is difficult to extrude, only being used in blends with LDPE to provide foam products with increased stiffness. LLDPE does not shear thin appreciably, has poor melt strength, and is difficult to process so it is used in blends with LDPE resins for crosslinked foam applications. Cellular, porous UHMWPE produced by non-foaming leaching techniques could be used as a substrate matrix in bone regeneration and in hip- and knee-joint replacements, being approved by the FDA for *in vivo* medical applications.

2.2 Other Grades

Affinity PO plastomers (POP) as sealants deliver an unparalleled combination of low seal initiation temperature, hot tack strength, seal-through contamination, toughness, tear resistance, and transparency. Affinity POP created using Insite technology are now used in many food packaging applications, such as fresh-cut produce, milk, fresh and processed meat, and bulk cheeses. They are replacing traditional sealant layers with a less costly structure that offers even higher performance in terms of optics, heat seal, hot tack, and low seal initiation for personal care products, such as detergents, powdered soaps, and shampoos, and for health and hygiene applications, especially where elasticity is required. They are used for flooring, containers, extruded profiles, and injection moulded items. A particular advantage of these applications is the reduced content of low molecular weight extractables in the plastomers and the very good organoleptic properties. In injection moulding, these materials are processed to form highly flexible lids and seals.

Dowlex PE resins offer toughness, puncture resistance or good tear resistance, higher performance, and processability, and have a wide variety of applications in blown and cast film, extrusion coatings, injection moulding, and rotomoulding. The impact resistance and hot tack strength of these materials provide a real advantage in food and speciality packaging. For hygiene films, Dowlex PE resins are often the materials of choice, as they are for agricultural applications like silage wrap and mulch

film. In addition to film processing, Dowlex PE resins can be extruded or moulded, and are the materials frequently preferred for pipes, membranes, and other durable goods.

For liquid, dry, and frozen foods, Elite enhanced PE resins reduce package thickness by up to 25% without sacrificing toughness or machinability. On high-speed stretch film lines, Elite enhanced PE resins can run faster and thinner without compromising their holding force. For lamination films, packers can maintain stiffness and toughness while reducing pack weight. Other film applications include baby nappy backing sheets and heavy-duty shipping sacks. These resins are compatible with a wide range of pigments and enable shorter production cycles for rotomoulded products such as toys and playground equipment. The products made from these resins can combine sealability and stiffness, high stretch and high puncture resistance, impact strength and processability, stiffness and impact strength, and many other unique combinations. In addition, these benefits can be applied to a wide variety of film, laminate, rotomoulded, and coated products.

2.3 Filled Grades of Polyethylene

PE has very low modulus and stiffness and consequently the improvement in mechanical properties achieved by the addition of fillers is not significant. Among PO, LDPE and HDPE display a most dramatic embrittlement when filled with dispersed materials. In the case of PE copolymers and especially UHMWPE, correlations between deformation and filler volume are smoother, yet they are different from the theoretical relationship. By choosing the appropriate filler, PE type, and compounding technology, it is possible to design products with properties approaching those of some engineering polymers. For these reasons, fillers are used not only to reduce polymer content and cost, but also to enhance the performance. In the case of HDPE, the critical size of the filler particles is in the range 0.5–2 μm .

Natural calcium carbonate improves viscosity, hardness, and some physicomechanical and electrical properties, and reduces shrinkage at forming. *Precipitated calcium carbonate* with a particle size of 0.5 μm improves thermal stability; use of 0.1 μm particle size gives good mixing, smooth surfaces, good gloss, and abrasion resistance; and use of 0.3 μm particle size imparts good dispersion and heat resistance. Extrusion, orientation, and laminating processes are used in the production of transpirable mineral-filled (with calcium carbonate) PE films and transpirable structures combining such films with non-woven fabrics by a Vaporweb process developed by Reifenhauser and BBA [4].

Carbon black, incorporated in amounts of 0.5–2.5 wt% in LDPE, HDPE, and ethylene-vinyl acetate (EVA), acts as a thermal and UV stabiliser, offering good thermal and ageing resistance. It imparts surface resistivity and increases tensile strength. It is used in cable compositions, and also for sheets, pipes, conduits, and injection moulded parts.

Glass spheres with diameters of 4–44 μm , together with coupling agents such as silanes, improve flow properties, give uniform shrinkage, and increase the modulus and the compression resistance. An HDPE masterbatch reinforced with 58 wt% long glass fibres is used in blow moulding.

Kaolin at 20–45% in LDPE enhances the abrasion resistance and the electrical properties. *Calcinated clay*, that diffuses light, is beneficial in ensuring light reaches ground level in greenhouses covered with LDPE or EVA films. *Montmorillonite nanoclays* are used in agricultural film because of the high specific infrared absorption without losing transparency and the mechanical properties.

Compounding with *mica* leads to excellent electrical and thermal properties and good dimensional stability. *Talc-filled PE* has a rapid injection cycle, good resistance, and a good control of flow is possible. *Vavonite* improves the surface gloss and moisture resistance.

2.4 Copolymers

2.4.1 Copolymers with alpha-Olefins or LLDPE

Commonly used comonomers are butene-1, hexene-1, octenes, etc. Octene LLDPE resins (density 0.920 g/cm³) were introduced in 2001 by Nova Chemicals Pittsburgh. They are made using the Advanced Sclairtech solution process and proprietary catalysts under the trade name of Sclair ASTute FP120. They are designed for use in premium film applications such as food and speciality packaging, laminations, coextrusions, and heavy-duty shipping bags. They exhibit excellent dart impact and puncture resistance, good tear strength, sealability, and optical properties, and have excellent melt stability for improved blow film processability.

2.4.2 Ethylene–Propylene Copolymers (Polyallomer)

These materials have better resistance to stress cracking than PE or PP, superior low-temperature toughness compared with PP or PE, better fatigue resistance than PP, and are of low density. The disadvantages are that crystallisation continues for 50 hours after moulding, and the low surface hardness. Applications include wire covering, film, and blow-moulded bottles.

2.4.3 Copolymers with Cyclo-olefins

These copolymers were discovered by Mitsui (ethylene-dimethanooctahydronaphthalene) in 1984 and the Celanese–Ticona group (previously Hoechst) (ethylene with norbornene (from dicyclopentadiene) in the presence of metallocenes) in 1990, with scale-up to pilot plant in 1993 and 1996, respectively. These copolymers permit a transmission of light of 92%, being more transparent than polycarbonate. Because of their barrier properties for humidity, they are ideal candidates for blister packaging for drugs (e.g., Bayer's aspirin drugs), are approved by the FDA for food packaging, and can also be used for the manufacture of disposable syringes, diagnostic sheets and ampoules, and lenses and optical materials. They are also used in printing.

2.4.4 Copolymers with Vinylic Monomers

Monomers containing polar functions are incorporated into PE for two main purposes: to influence the crystallisation process or to act as polar 'crosslinks'. The addition of increasing amounts of polar comonomers serves to reduce the overall degree of crystallinity of the resin, with an accompanying decrease in stiffness. Polar comonomers also inhibit the formation of spherulites resulting in clearer products due to reduced scattering of light. Copolymers that form polar crosslinks with the aid of cations fall into the general category of ionomers. Polar crosslinks stiffen the non-crystalline regions of ionomers, maintaining their moduli at useful levels even when samples contain negligible crystallinity. Of commercial importance are the copolymers of ethylene with vinyl acetate (EVA) and methacrylic acid (MA).

EVA copolymers are clear, flexible (rubbery), soft materials with high tensile strength and are primarily used in packaging and adhesive applications. EVA copolymers have improved low-temperature flexibility (–70 °C) compared to LDPE, good chemical resistance, and high friction coefficients. Films have improved clarity and weathering resistance compared to LDPE. Similar flexibility to plasticised polyvinyl chloride (PVC) may be obtained, but without the problems of plasticiser migration. They may be crosslinked and radio frequency welded. They have better tear resistance than LDPE and can accept high filler loadings. The disadvantages are a reduced chemical resistance compared to LDPE, reduced barrier properties, and reduced creep resistance.

Applications include stretch film for shrink-wrapping, protector strips, shoe soles (crosslinked), disposable medical equipment, flexible toys, tubing, wire coating, and heat-sealing coatings on PP,

polyethylene terephthalate (PET), and aluminium foils. EVA with 12% VA exhibits lower water absorption and cost, and higher tensile strength, permeability, modulus, and dielectric strength than EVA with 25% or 33% VA. It has lower heat-seal strength and flexibility and poorer low-temperature performance compared with EVA containing 25% or 33% VA. It is preferred for food packaging, cable sheets, O-rings, seals, and rail pads. Heat-seal strength improves with VA content, as do flexibility and low-temperature performance. Increasing the VA content decreases tensile strength, resistance to heat deformation and chemicals, and barrier properties. EVA with 33% VA is useful in cable sheaths, hose, sheet, ring seals, protective caps, clips, cable binders, infusion bottles, lids, all kinds of closures, flexible panels, bellows, rail pads, and O-rings.

Commercial EVA copolymers are available with VA concentrations of up to 27 mol% (55 wt%). Copolymers containing in excess of approximately 25 mol% VA are essentially amorphous (see Table 2.2).

Vinyl acetate content (mol%)	Melting range (°C)	Degree of crystallinity (X-ray diffraction) (%)
4.3	83–103	27.4
7.6	72–98	19.9
16.8	61–77	8
27.0	41–44	Non-crystalline

EVA copolymers and LLDPE copolymers follow the same relationship of modulus as a function of increasing total branch content and decreasing degree of crystallinity, hardness, and yield stress. The tensile impact and puncture strength increase with co-unit content. The VA content improves the ESCR relative to LDPE.

Ethylene–vinyl alcohol (EVOH) copolymers are hydrolysed derivatives of EVA copolymers (alcoholic sodium hydroxide or potassium hydroxide in an organic solvent solution at high temperature). They are stiffer than their precursors, are somewhat less clear, and have good oxygen barrier properties. Ethylene ionomers (neutralised ethylene–MA and ethylene–acrylic acid copolymers) are soft, clear, have high tensile strength, and are abrasion and oil resistant. In EVOH copolymers the PE unit cell is not disrupted. The melting and softening properties are close to those of LDPE and higher than those of EVA copolymers.

2.4.5 Ethylene Ionomers

These include two groups, one based on an ethylene–MA copolymer and the other on sulfonated ethylene–propylene–diene terpolymer. As for EVA copolymers, they are synthesised at high pressure. The incorporation of polar branches occurs essentially at random. Ionomers are produced from base resin by reaction in the molten state of the acid functionalities with hydroxides of such metals as caesium, calcium, lithium, sodium and zinc, the latter two being the ones frequently used in practice. The maximum concentration of acid is 6 mol%. In the solid state they behave as rubbers that are lightly crosslinked, i.e., thermoplastic elastomers. They have exceptional optical clarity, are resistant to diffusion of oils, greases, and fats, and are readily heat-sealable. Because of these properties they have found use in meat packaging applications. The combination of good adhesion to many substances including glass and metal, high tensile strength, and good puncture and abrasion resistance means ionomers are suited for encapsulation of chemical reagent bottles.

Elastomeric ionomers based on the sulfonation of chlorinated PE were introduced by DuPont during the early 1950s. Curing of these materials with various metal oxides gives rise to a combination of ionic and covalent crosslinks and these elastomers are commercially available under the trade name Hypalon.

Ethylene-carbon monoxide polymers offer superior performance as high-strength fibres for aramide tyre cord, but at a significantly lower cost. Their structure is more compatible with rubber than steel, polyester, or PA tyre reinforcements.

2.4.6 Block and Graft Copolymers [6]

Functionalised PO as block and graft copolymers used as compatibilisers or to increase interactions with other materials are prepared by free radical grafting (the simplest method), metallocene-catalysed copolymerisation of olefins with functional monomers, or anionic polymerisation (silane-containing PO). They are also produced by controlled/living polymerisation techniques such as nitroxide-mediated controlled radical polymerisation, atom transfer radical polymerisation (ATRP), and reversible addition-fragmentation chain transfer (RAFT).

2.4.7 Primacor Copolymers

Under harsh packaging conditions, Primacor copolymers provide lasting adhesion to aluminium foil and other polar substrates. They are widely used in extrusion coating to produce the laminates used for cartons, pouches, and tubes, and the shielding for wires and cables. Primacor copolymers not only protect pack contents, even for challenging filling goods such as powders, oils, and liquids, but they also provide package integrity through their resistance against seal or interlayer delamination, tears, and punctures. With good clarity and low taste/odour pick-up they are widely used for pouches and aseptic liquid boxes. They are also used in toothpaste tubes and other flexible packages that require seal strength and security.

Primacor copolymers are specifically designed for high performance and offer particular benefits as sealants in the packaging of fatty and greasy products. High acid Primacor products also deliver tremendous adhesive characteristics in solvent-free dispersions.

2.4.8 Chlorinated Polyethylene (CPE)

CPE exhibits a good UV and chemical resistance, high tear strength, is flexible, and difficult to ignite. Among the disadvantages is the evolution of hydrogen chloride during combustion and high gas permeability.

2.5 Blends [7]

The broad spectrum of structures, properties, and application of PE can be further broadened by blending. Properties that PO generally contribute to polyblends include high melt strength and elasticity, viscosity and shear sensitivity, low polarity, dielectric constant, and loss, and water repellency. PE of different densities are generally miscible in the melt. Upon cooling, UHMWPE, HDPE, and LLDPE are isomorphous and co-crystallise to a homogeneous product. HDPE, MDPE, and LDPE show interesting synergism.

Major commercial blends of PE include the addition of low-molecular-weight PE (LMWPE) to high molecular weight PE (HMWPE) to improve processability, addition of LDPE to LLDPE to improve processability, incorporation of PA in HDPE for impermeability, incorporation of 2–4% maleated ethylene propylene diene terpolymer (EPDM) and other PO in PA and other engineering thermoplastics for impact strength, incorporation of CPE and EVA in PVC as impact modifiers or plasticisers, and the growing use of CPE and maleated PO as compatibilisers for other blends [8]. PO/PS blends permit easy fibrillation, being used to produce fibril or opaque, tough, and waterproof synthetic paper. PO/PET blends give self-texturing fabrics. The barrier properties of PE are often improved by combination with EVOH, polyvinylidene chloride, and PA, either by blending or by laminating. Blends of PO with PA or polycarbonates permit balanced control of permeability and

water absorption. PE in polycarbonates improves melt flow and energy absorption for automotive applications. Addition of PE powder to other polymers has been recommended to increase surface lubricity and abrasion resistance. Addition of ethylene copolymers to PE has been used to improve toughness, and impact and chemical resistance, while addition of CPE to PE helps in reducing flammability. A crosslinked blend of PE and butyl rubber improves mouldability and resistance to compression set. Lignin acts as an inert filler for PE but it does not cause stiffening as do other particulate fillers such as calcium carbonate or carbon black [9]. Styrene–butadiene–styrene and styrene–isoprene–styrene block copolymers have been added to LLDPE to increase flexibility, tear and impact strength, and low-temperature flexibility. PE increases melt processability of the autofluff fraction helping processing [10].

PE bottles exhibit a very poor gasoline permeation resistance, where about 25% of the filled gasoline penetrates out of a PE bottle in 14 days at 40 °C. Xylene, white spirit, cleaning naphtha, and many other pure and/or mixed hydrocarbon solvents easily penetrate PE containers: such permeation results in pollution, safety, and health problems. The laminar blends of PE and PA, polyvinyl alcohol, and/or EVOH (with 32% ethylene), in the presence of modified PA or zinc-neutralised ethylene–acrylic acid copolymer as compatibilisers, exhibit significantly higher barrier properties as compared with PE or the conventional homogeneous blends associated with uniform dispersed PA within a PE matrix [11].

PET/PE composites in an *in situ* fibre formation are used for compatibilisation of PET– ϵ -caprolactone copolymers.

PE/cellulose or scrap paper cellulose fibres, LDPE/plasticised starch, and 40% wood-filled HDPE are found to increase breaking strengths, impact properties, and heat deflection temperature, in addition to reducing water absorption.

Other interesting blends containing PE are natural rubber/PE, PP/UHMWPE, polyvinylidene fluoride (PVDF)/UHMWPE, PE/EVA, PE/PVC, PE/liquid crystalline polymer (Vectra), and styrene–isoprene–styrene block copolymers with ULDPE [12] with good puncture resistance (>100 kN/m).

2.6 Composites

Examples of PE-containing composites are hydroxyapatite-filled PE composites, HDPE/wood flour or HDPE/wood flake, UHMWPE/gold, HDPE/layered silicate nanocomposites, and nanocomposites comprising HDPE, organically modified clay, and maleated PE.

PE/hydroxyapatite (hydroxyapatite is the main inorganic component of human bone) composites are produced by extrusion compounding and subsequent injection moulding. Shear-controlled orientation in injection moulding induces a strong anisotropic character.

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3 Properties

Table 3.1 Some properties of various grades of PE						
ASTM or UL test	Property	LDPE	LLDPE	MDPE	HDPE	UHMWPE
Physical						
	Usual appearance, film products	Transparent	Transparent		Translucent to opaque	
	Usual appearance, solid products	Hazy to opaque			Hazy to opaque	
	Elastic behaviour	Flexible, resilient		Flexible, resilient	Flexible, resilient	
D792 [1]	Density (g/cm ³)	0.917–0.94	0.915–0.95		0.95	0.93–0.95
	Glass transition temperature (°C)	–110	–110		–110	
	Ductile/fragile temperature (°C)	–70	–70	–70	–70	
	Maximum operating temperature (°C)	50	50	50	55	
D792	Specific volume (cm ³ /g)	1.10-1.08		1.08-1.06	1.06-1.04	1.06
	Mould shrinkage (%)	3	3	3.5	3	4
	Mould temperature range (°C)	20–40	20–60	20–60	30–70	
D570 [2]	Water absorption, 24 h (%)	0.005–0.015	0.005–0.01	0.01	0.005–0.01	0.005–0.1
	Pyrolysis behaviour	Becomes clear, melts, decomposes, vapours are barely visible	Becomes clear, melts, decomposes, vapours are barely visible	Becomes clear, melts, decomposes, vapours are barely visible	Becomes clear, melts, decomposes, vapours are barely visible	
	Ignition behaviour	Continues to burn after ignition, yellow flame with blue centre, burning droplets fall off, slight paraffin-like odour	Continues to burn after ignition, yellow flame with blue centre, burning droplets fall off, slight paraffin-like odour	Continues to burn after ignition, yellow flame with blue centre, burning droplets fall off, slight paraffin-like odour	Continues to burn after ignition, yellow flame with blue centre, burning droplets fall off, slight paraffin-like odour	
Mechanical						
D638 [3]	Tensile strength (MPa)	10–17	20	14	20–35	21
D638	Tensile modulus (MPa)	96–262		172–379	413–1241	137–758
D638	Tensile elongation at yield (%) (elongation at break (%))	600 (200–600)	(500)	(300–1000)	900 (150)	200–500
	Strain at yield (%)	19	20	16	15	

Table 3.1 Continued ...						
ASTM or UL test	Property	LDPE	LLDPE	MDPE	HDPE	UHMWPE
D790 [4]	Flexural modulus (GPa)	0.245–0.335	0.35	0.60–1.15	0.75–1.575	1–1.7
D695 [5]	Compressive strength (MPa)					14
D785 [6]; D2240 [7]	Hardness, Shore D	D41–D50	55–56		D69 D55–D90	D62–D66
	Hardness, Rockwell R	10		15	65	67
	Hardness, Rockwell M	1	1		1	1
	Young's modulus	0.13–0.3	0.266–0.525		0.5–1.1	0.3–0.6
D256 [8]	Izod notched impact (kJ/m)	No break; >1.06	>1.06	0.14	0–150	No break
	Toughness, Izod notched impact at room temperature (J/m)	999	54–999	–	20–220	999
	Toughness, Izod notched impact at low temperature (J/m)	240–694	294–970	–	–	–
	Surface hardness	SD48 (42–50)	SD48	SD50	SD68 (62–69)	
Thermal						
D696 [9]	Coefficient of linear thermal expansion, (m/m/°C) 10 ⁻⁵ in/in/°F	(20)	(20)	(18)	(12)	11.1
	Specific heat (kJ/kg/K at 25 °C)		2.315		2.22–2.3	
D648 [10]	Heat distortion (deflection) temperature at 0.45 MPa (°F/°C); 1.80 MPa (at 0.45 MPa; 1.80 MPa (°C))	110/38; (50; 35)	45/7; 37/3	(62; 43)	(75; 46)	203/95
D3418 [11]	Melting temperature (°C)	105–120	220–260/105–120 (depends on branching)	105–120	120–130	
	Max. operating temperature (°C)	71			82	82
C177 [12]	Thermal conductivity (BTU in/ft ² /h/°F (10 ⁻⁴ cal/cm/s/°C))		3.37 × 10 ⁻³ W/m/°C		4.63–5.22 × 10 ⁻³ W/m/°C	2.92 (10.06)

Table 3.1 Continued ...						
ASTM or UL test	Property	LDPE	LLDPE	MDPE	HDPE	UHMWPE
UL94 [13]	Flammability rating	HB	HB	HB	HB	HB
	Fire resistance (LOI) (%)	17–18	17–18		17–18	17–18
	Oxygen index (%)	17	17	17	17	
Electrical						
D149 [14]	Dielectric strength (V/mil) short time, 1/8 in thick (MV/m)	(27)	(25)	(27)	(22)	900
D150 [15]	Dielectric constant	2.3 at 1 kHz	2.3 at 1 kHz	2.3 at 1 kHz	2.3 at 1 kHz	2.3 at 50 kHz
D150	Dissipation factor	$(3-4) \times 10^{-4}$ at 1 kHz	0.0003 at 1 kHz	0.0006 at 1 kHz	$(3-20) \times 10^{-4}$	0.0002 at 50 kHz
D257 [16]	Volume resistivity at 50% RH	16 log Ω cm	16 log Ω cm	18 log Ω cm	17 log Ω cm	$>5 \times 10^{16}$ Ω cm
D495 [17]	Arc resistance (s)	135-160		135-160		
Optical						
D542 [18]	Refractive index		1.51	1.52	1.54	
D1003 [19]	Transmittance (%)		4–50	4–50	10–50	
D1003	Haze (%)	1.3–27.5	0.8–28	2–40	6	
D523 [20]	Gloss (%)	35–97	32–85	7.9–10.1	5–120	
Radiation resistance						
	Gamma radiation resistance				Fair	Fair
	UV light resistance	Fair	Fair		Poor	Fair
Service temperature						
	Ductile/fragile temperature (°C)	–70	–70		–70	
	Heat deflection temperature at 0.46 MPa (°C)	40–50			60–90	68–82
	Heat deflection temperature at 1.8 MPa (°C)	30–40			45–60	40–50
	Max. continuous service temperature (°C)	80–100	90–110		100–120	67–82
	Min. continuous service temperature (°C)	–70	–70		–70	–30

Table 3.1 Continued...						
ASTM or UL test	Property	LDPE	LLDPE	MDPE	HDPE	UHMWPE
Other properties						
D543 [21]	Chemical resistance	Attacked by strong acids; unaffected by strong alkalis, dilute alkalis, and dilute acids	Attacked by strong acids; unaffected by strong alkalis, dilute alkalis, and dilute acids	Attacked by strong acids; unaffected by strong alkalis, dilute alkalis, and dilute acids	Attacked by strong acids; unaffected by strong alkalis, dilute alkalis, and dilute acids	
D543	Solvent resistance	Soluble in some aromatics above 60 °C	Soluble in some aromatics above 60 °C	Unaffected below 80 °C	Unaffected below 80 °C	
	Sterilisation resistance (repeated)				Poor	
	Thermal insulation (thermal conductivity) (W/m/K)	0.32–0.35	0.35–0.45		0.45–0.5	
<i>HB: horizontal burn (Underwriters Laboratories Inc. specifications)</i> <i>UL: Underwriters Laboratory</i> <i>RH: relative humidity</i> <i>Data taken from [22] and Plascams (Rapra Technology, Shrewsbury, UK)</i>						

Polyethylenes (PE) are semi-crystalline materials with excellent chemical resistance, good fatigue and wear resistance, and a wide range of properties (due to differences in structure and molecular weight). PE are easy to distinguish from other plastics because they float in water. Their properties permit both their identification and differentiation from other polymeric materials and also determine the end use of the products made from them. PE provide good resistance to organic solvents, degreasing agents, and electrolytic attack. They are resistant to water, acids, alkalis, and most solvents. They have a higher impact strength but lower working temperatures and tensile strength than polypropylene (PP). They are of low weight, are resistant to staining, and have low moisture absorption rates. The mechanical and thermal properties of PE, a viscoelastic material, are dependent on structure, molecular weight and its distribution, crystallinity and the type and amount of comonomer, temperature, and stress. Long-chain branches are important in the structure of low-density PE (LDPE). The size of long branches increases with increasing number average molecular weight (M_n) of PE, but the mean size of long branches relative to M_n decreases with increasing molecular weight. Logarithmic plots of storage modulus (G') versus loss modulus (G'') strongly depend on the molecular weight distribution (MWD) and the degree of side-chain branching, but are only weakly sensitive to temperature and weight average molecular weight (M_w).

The properties of most known commercial grades of PE differing by structure and density are given in Table 3.1.

The properties of PE depend on a great number of factors such as molecular structure, tacticity and composition of copolymers and modified polyolefins, molecular weight and MWD, morphology, environment, and so on.

3.1 Density

The density of PE depends on the polymerisation process used and on the thermal history of each sample (Figure 2.1 and Table 3.2). It markedly influences the properties and represents the main property used in the classification of PE grades (see previously). The density of a 100% crystalline sample is considered as 1 g/cm³, while that of a 100% amorphous sample is 0.85 g/cm³.

Elastomer-modified, filled, or reinforced grades might have significantly higher density depending on their formulation. For example, a high-density PE (HDPE) grade with 40 wt% calcite has a density of 1400 kg/m³, while crosslinked HDPE with 30 wt% wood flour has a density of 1032 kg/m³. The density of LDPE filled with 50 wt% CaCO₃ is 1184 kg/m³.

PE is a linear hydrocarbon polymer. Some grades contain short and/or long branches, and some or no unsaturation. The melting point of HDPE ranges from 120 to 130 °C.

The detailed nature of structure–property relationships is a very complex issue and is not within the scope of this book. Further details can be found in many textbooks [23-25]. Structure, molecular weight, MWD, crystallinity, etc., significantly influence the properties of PE and, hence, are discussed briefly here.

3.2 Molecular Weight and Molecular Weight Distribution

Melt flow rate (MFR) is commonly used to measure the viscosity of a melt and is defined as the weight of a polymer melt that can be extruded through a defined orifice in a given time at a defined temperature and pressure. It is inversely related to M_w . Easy flowing grades are generally less tough than those of higher M_w and stiffer flow. PE, a crystallising polymer, is soluble only at elevated temperatures. Since most methods for determining molecular weight and MWD require the dissolution of the polymer, these determinations must also be carried out at elevated temperatures, certain modifications to the conventional methods being used for determining molecular weights. The methods for measuring molecular weight and characterising MWD of PE include classic methods, such as light scattering, osmometry (with special semi-permeable membranes to withstand high temperatures, such as cellophane and Ultracella filters), viscometry, and fractionation, and also newer ones, such as temperature rising elution fractionation (TREF) and the combination of size exclusion chromatography (SEC) with various molecular weight sensitive detectors.

Some useful data for such measurements are given in Tables 3.2 and 3.3. PE are soluble only in the vicinity of their crystalline melting points, generally >100 °C, where they are susceptible to thermo-oxidative degradation. Temperatures of about 120–140 °C are normally used with HDPE. Ultra high molecular weight PE (UHMWPE) is especially slow to dissolve. The most suitable solvent is nitrogen-sparged, stabilised (0.1% Santonox R) Decalin; the solution components are shaken gently under nitrogen for an hour at 180 °C. Filtration is conducted at 180 °C using polytetrafluoroethylene (PTFE) filters under nitrogen.

A sealed capillary viscometer under inert atmosphere is recommended for viscosity measurements. Selected Mark–Houwink parameters are given in Table 3.3. Mark–Houwink equations are not applicable to high-pressure LDPE containing long branches.

The simplest method for estimating the MWD from fractionation data (Table 3.4) is to plot the weight of the fraction against the value of the molecular weight of each fraction – integral distribution. The molecular weights of the fractions are determined using osmometry (MO), light scattering (LS), or viscosity. The derivative of the curve obtained, dw/dM , when plotted against molecular weight gives the differential distribution. Typical TREF curves for HDPE and ethylene–propylene copolymer are shown in Figure 3.1.

Solvent	λ (nm)	Temperature ($^{\circ}\text{C}$)	dn/dc (ml/g)
1-Chloronaphthalene	436	135	-0.215
	546	135	-0.192
	633	135	-0.183
1,2,4-Trichlorobenzene	436	135	-0.125
	546	135	-0.110
	633	135	-0.107
<i>n</i> -Decane	436	135	0.117
	546	135	0.114
	633	135	0.112

Solvent	Temperature ($^{\circ}\text{C}$)	K ($\times 10^3$ ml/g)	a	Method
Decalin	135	62	0.70	LS
1,2,4-Trichlorobenzene	135	52.6	0.70	LS/MO
1,2,4-Trichlorobenzene	130	39.2	0.725	LS/MO
1-Chloronaphthalene	130	55.5	0.684	LS/MO
Tetralin	130	51	0.725	MO
1,2-Dichlorobenzene	138	50.6	0.7	LS
Xylene	75	1.35	0.63	MO

LS: light scattering
MO: osmometry

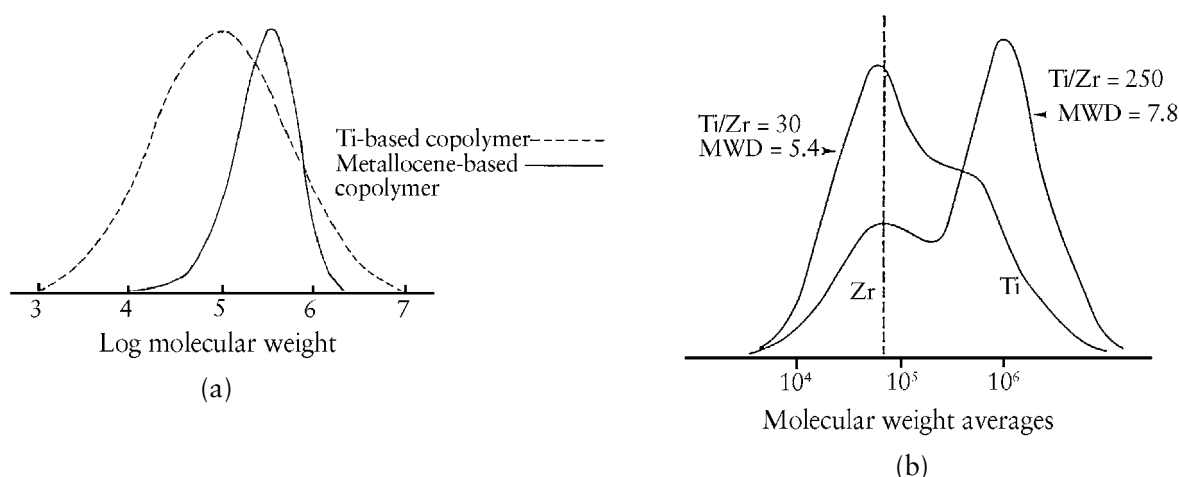


Figure 3.1 (a) Distribution of molecular weights for ethylene–propylene copolymers from isospecific metallocenes; (b) gel permeation chromatography elution curves for HDPE produced with CpTiPh_2 and Cp_2ZrCl_2 mixtures. Cp = cyclo-olefins [23]

Redrawn from *Handbook of Polyolefins: Synthesis and Properties, 2nd Edition, Ed., C. Vasile, Marcel Dekker, New York, NY, USA, 2000. Copyright Marcel Dekker, 2000.*

Table 3.4 Solvent and/or solvent–nonsolvent combinations for fractionation of polyethylenes

Solvent and/or solvent–nonsolvent	Method
2-Ethylhexanol–Decalin (85:15)	Precipitation at low temperature
Tetralin–benzyl alcohol (60:40)	Precipitation by decreasing temperature, 165–105 °C
Toluene– <i>n</i> -butanol	Precipitation by decreasing temperature, 115–100 °C
Xylene–triethylene glycol	Precipitation
Xylene–polyoxyethylene	Precipitation by decreasing temperature, 130–175 °C
Tetralin–2-butoxyethanol	Column elution at 128 °C
Tetralin	Column extraction, variable temperature
Xylene–diethylene glycol–monoethyl ether	Column elution, 126 °C
<i>o</i> -Dichlorobenzene	Size exclusion chromatography, 130–138 °C
1,2,4-Trichlorobenzene	Size exclusion chromatography, 135 °C

An increase in molecular weight leads to an increase in melt viscosity and impact strength. A change in crystallinity also affects the bulk properties.

Viscometry is performed according to ASTM D4020 [26]. For UHMWPE the solvent may be decahydronaphthalene and the relationship is $[\eta] = 53,700 \times [M_w]^{1.37}$. Measurements of molecular weight by solution viscosity are only accurate for virgin UHMWPE powder that has not been subjected to temperatures above its crystalline melting point (138–142 °C) to avoid insolubility.

High-temperature (130 °C) SEC, although a relative method requiring calibration, is the most commonly used method to establish the molecular mass of these polymers. However, few SEC calibration standards are commercially available for the calibration of high-temperature SEC. Molecular mass fractions of low polydispersity, M_w/M_n , of less than 1.2 are the most useful for calibrating SEC. The US National Institute of Standards and Technology (NIST) PE standard reference materials (SRM) are the only available narrow fractions of PE. Prior to the availability of these standards, crude approximations had to be used in the calibration of gel permeation chromatography for mass distribution measurements. Reference material (RM) 8456, an orthopaedic-grade UHMWPE, became available in October 2000. RM 8456 is intended primarily for use in mechanical characterisation of material properties and laboratory-simulated performance of orthopaedic joint replacement implants. The availability of this reference PE is expected to aid in the development of improved test methods and materials by providing a benchmark for comparisons. The need for this reference biomaterial was identified at a workshop held at NIST and its development was the result of collaboration among a materials supplier, the orthopaedic research community, and NIST. The material used to prepare RM 8456 was donated by Poly Hi Solidur Inc., MediTECH Division (Fort Wayne, IN, USA) in a form similar to that from which many orthopaedic components are machined: a cylindrical bar with nominal dimensions of 7.62 cm in diameter. Reference properties, reported as mean values with their expanded uncertainties, are Young's modulus, tensile yield strength, tensile ultimate strength, and tensile elongation-to-failure. These properties characterise the bar across the central 5.62 cm of its diameter and down the entire bar length. Material beyond the central 5.62 cm is found to differ significantly from that within. Published data indicate that molecular weight ranges are $M_n = 37,000$ – $1,500,000$ and $M_w = 120,000$ – $600,000$, with values of polydispersity $M_w/M_n = 3$ – 9 or higher up to 15.

3.3 Crystallinity

PE is a crystallisable polymer. Since chains may be entangled or otherwise imperfect (branching, comonomers, structural defects, etc.), the structure is not completely regular, and hence PE is best described as a semi-crystalline polymer. Many of the properties of PE and most of its properties

below the melting point depend largely on its crystalline content, which in turn depends essentially on the number of branches rather than their length. Crystallinity in PE is primarily a function of the number of branches along the chain. As more branches are introduced, disruption becomes greater and crystallinity decreases rapidly. At an extremely high degree of branching, PE would become an amorphous material. Long-chain branching can be ignored with respect to the properties below the melting point. LDPE has about two branches per hundred carbon atoms and a crystallinity of about 50%. Polymerisation conditions can change the degree of branching, however, and the crystallinity may be varied from about 35 to 75%. In HDPE there can be from about 0.5 to practically zero branches per hundred carbon atoms, so that the crystallinity may vary from 60 to 90%.

It is usually more convenient to refer to the density rather than to the crystallinity. These quantities are connected by the linear relationship:

$$c = \frac{d_c(d - d_a)}{d(d_c - d_a)}$$

where c is the weight percent crystallinity, d is the measured density, d_a is the amorphous density (0.85 g/cm³), and d_c is the crystalline density at the given temperature. Density can be determined very rapidly and accurately using a density-gradient column, while the measurement of crystallinity requires X-ray techniques. The properties of PE are generally correlated to density rather than crystallinity.

The degree of crystallinity and crystal structure depend on the thermal history. A rapid quenching gives a tough and clear product since it suppresses the formation of crystals, while annealing or slow cooling leads to a rather brittle and hazy product. Increased crystallinity increases hardness, modulus, strength, abrasion and wear resistance, creep resistance, barrier properties, shrinkage, and density. Low crystallinity offers good processability, better transparency, economical melt processing, and good thermoforming capability. Depending on the processing conditions, 65–95% crystallinity in the finished product can be achieved. Crystallinity as well as melting and glass transition temperatures (T_g) can be measured using differential scanning calorimetry (DSC) (Figure 3.2).

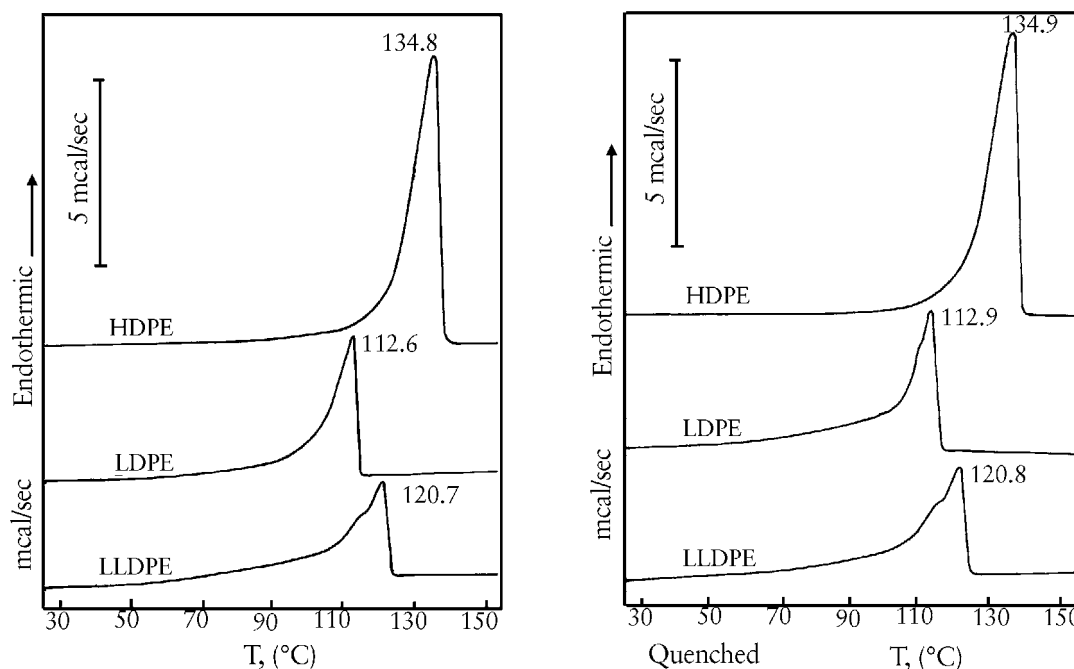


Figure 3.2 Typical DSC curves for different grades of PE showing the effect of cooling rate on the formation of crystalline structure [27]

Redrawn with permission from C. Price, The Rapra Collection of DSC Thermograms of Semi-crystalline Thermoplastic Materials, Rapra Technology, Shrewsbury, UK, 1997. Copyright Rapra Technology, 1997.

The morphological structure in an injection moulded article can be quite complex, with layers of different crystallinity, the detailed crystalline structure depending on the shape of the article and the conditions under which it is moulded. Thicker sections in a moulding or extrusion may vary in crystallinity, with the rapidly cooled surface having a tough skin, while the slower-cooling interior has larger spherulites and is relatively brittle. Consequently, moulding shrinkage, internal stresses, dimensional stability, and warpage depend on the crystalline structure. The size of spherulites in PE may vary from 11 to 20 μm (determined by polarised light microscopy). The use of nucleating agents can further modify the crystallinity and crystalline structure by providing numerous sites for growth of small spherulites during cooling from the melt. This technique is used in injection moulding to improve clarity and rigidity and to reduce set-up time.

3.3.1 Melting

The enthalpy of melting (ΔH_u) ranges from 192 to 218 J/g or $(\Delta H_u)_{100} = 960\text{--}980$ cal/mol. The equilibrium melting temperature (T_m) = 138–146 °C (the most used value is 145.5 °C).

The physical properties of PE related to crystallisation are crystal density (1.00 g/cm³), amorphous density (0.855 g/cm³), and crystallisation temperature (T_c) from 87–89 °C from solution (xylene) to 112–130 °C from melt (for HDPE).

Using the example of PE crystals, three reversible processes can be distinguished which may involve additional latent heats:

- (i) the conformational motion of large amplitude, which increases the heat capacity beyond the baseline of the vibrational contribution and may lead to changes in the interface structure;
- (ii) the melting of small segments of macromolecules (or oligomers) below a critical length; and
- (iii) the melting of long segments of macromolecules that have a melting temperature within the main melting peak, but need no molecular nucleation due to partial melting [28].

3.3.2 Orientation

PE may be oriented either in the melt phase or by stretching when it is solid. In both processes the polymer chains are aligned in the perfect direction usually along the line of flow or stretch. Deliberately introduced orientation in fibres or films can lead to dramatic changes in molecular and crystallite arrangements, so that major variations in the properties of the article can be expected. Orientation produced by stretching increases tensile strength and reduces elongation in the direction of stretch. Biaxial orientation of PE films improves clarity.

3.4 Thermal Properties

Unlike metals and other inorganics, plastics are extremely sensitive to changes in temperature. The mechanical, electrical, or chemical properties of plastics cannot be considered without knowing the temperature at which the values are obtained. The thermal properties of a polymer typically determine its low- and high-temperature applications, impact properties, and processing characteristics. Generally, temperature limitations of PE range between –180 and +90 °C. HDPE has superior heat resistant characteristics (up to 900 °C).

PE can be used at low temperatures, –18 °C or less, without risk of brittle failure. Thus, a major application for certain PE piping formulations is low-temperature heat transfer applications, such as radiant floor heating, snow melting, ice rinks, geothermal ground source heat pump piping, and compressed air distribution. The applications where high-temperature properties of PE are of particular interest include sterilisation (particularly steam sterilisation), microwave ovenproof

containers, and parts of dishwashers and washing machines that are subjected to hot water in the presence of detergents.

Scapa North America (Windsor, CT, USA) has introduced Duofoam VJ series of double-coated PE foam tapes, in order to provide superior performance in high-temperature bonding and mounting applications where heat resistance is critical. Double coated with a high-performance, pressure-sensitive adhesive system, Duofoam VJ series products provide excellent holding power and good tack, and bond well to a wide variety of surfaces including metals and engineered plastics. The products offer very good long-term ageing, resistance to environmental extremes, and high performance over a range of operating temperatures. The closed-cell PE foam used for Duofoam VJ series tapes does not absorb water and provides good thermal insulation properties. These products are ideally suited for industrial wire harness, insulation, gasketing, spacing, and sound attenuation applications.

The Plastics Pipe Institute's High Temperature Plastics Division produces resins and pipe or tubing for specialised applications. These products provide distinct characteristics not found in other plastic pipe, most particularly resistance to temperatures with continuous use ratings as high as 150 °C, and pressure ratings as high as 1105 kPa. Among these products, one can mention crosslinked PE (XPE) and XPE–aluminium–XPE (XPE-AL-XPE). XPE and XPE-AL-XPE are used to produce pipe and tubing for domestic hot and cold water applications. They offer the advantages of plastics, including overall durability, low weight, corrosion resistance, and flexibility. In addition, they are capable of resisting the temperatures and pressures encountered in domestic hot water systems.

XPE-AL-XPE capitalises on the corrosion and chemical resistance of the plastic and the pressure capacity of the metal by laminating the aluminium layer between layers of plastic. XPE-AL-XPE does not corrode, and resists most acids, salt solutions, alkalis, fats, and oils. It is widely used throughout North America in residential and commercial plumbing, municipal water service lines, residential and industrial heating, and compressed air and compressed gas systems.

XPE maintains a good hydrostatic rating at 92 °C, and resists creep when projected to a 50-year service life. For plumbing, XPE is limited to 82 °C. In case of emergency, XPE can also withstand higher temperatures for short periods of time. It is widely used in hydronic heating systems for radiant heating, snow and ice melting, general hydronic piping, and even in ice rinks and refrigeration warehouses. Other advantages include the fact that it is safe, complying with potable water health effects standards at all pH levels; it is freeze-tolerant, with the ability to expand and contract, thus avoiding costly repairs of ruptured pipes; and the elimination of corrosion problems.

Specific volume (v_{sp}), thermal expansion coefficient, heat capacity at constant pressure (c_p), heat capacity at constant volume (c_v), enthalpy, entropy, and thermal conductivity (λ) are thermal characteristics relevant for processing and applications. They depend on PE grade, temperature, pressure, average molecular weight, branching, crystallinity or density, stretching ratio, heating rate, spherulite size, and so on.

3.4.1 Specific Volume

Values of specific volume for different grades of PE at different temperatures and pressures are given in Table 3.5.

3.4.2 Specific Heat

The specific heat of PE is higher than that of PP; therefore the plasticising capacity of an injection moulding machine using PE is lower than that using PP. The plasticising capacity is defined as the amount of material that can be melted and plasticised in the barrel of a given injection moulding machine in a given time.

Table 3.5 Specific volume ($10^3 \text{ m}^3/\text{kg}$) of HDPE and LDPE at various temperatures and pressures					
Temperature ($^{\circ}\text{C}$)	Pressure (MPa)				
	0.1	10	40	100	200
HDPE					
19.5	1.021	1.019	1.013	1.002	0.986
32.3	1.026	1.023	1.017	1.005	0.989
55.8	1.034	1.032	1.024	1.011	0.992
76.4	1.043	1.040	1.031	1.016	0.996
94.5	1.053	1.049	1.039	1.023	1.000
115.4	1.072	1.067	1.055	1.035	1.010
128.9	1.103	1.093	1.069	1.040	1.015
142.0	1.269	1.257	1.228	1.058	1.027
165.4	1.292	1.278	1.246	1.200	1.031
180.9	1.308	1.293	1.358	1.209	1.158
199.7	1.327	1.311	1.273	1.221	1.167
LDPE					
19.0	1.072	1.069	1.059	1.043	1.021
28.9	1.078	1.074	1.064	1.046	1.023
51.2	1.092	1.088	1.075	1.054	1.028
79.5	1.127	1.120	1.101	1.071	1.039
97.9	1.160	1.150	1.126	1.092	1.052
116.4	1.233	1.207	1.154	1.103	1.055
135.1	1.269	1.258	1.229	1.154	1.095
142.7	1.276	1.264	1.234	1.191	1.104
160.5	1.293	1.280	1.248	1.202	1.152
184.8	1.316	1.301	1.265	1.216	1.162
198.0	1.327	1.311	1.273	1.221	1.168

The specific heat is a function of temperature. A significant rise in the specific heat is observed near the melting point (Figure 3.3).

Specific heat and enthalpy control the cooling of an article in a mould and predominantly the design of the cooling channels in a mould. The cooling system should balance the heat flow from the part to ensure uniform part cooling and minimise residual stresses, differential shrinkage, and warpage.

Specific heat depends on the crystallinity of a sample (Figure 3.4).

The heat capacity at constant pressure (c_p), at various temperatures, is given in Table 3.6.

3.4.3 Glass Transition Temperature and Melting/Crystallisation Temperature

The mechanical properties of PE at a particular temperature are dependent on the T_g . At very low temperatures, the macromolecules are largely immobile. As the polymer is heated, the restricted macromolecular zones become progressively more mobile. At the T_g , the material changes from a glassy hard state to a soft tough state because certain molecular segments become more mobile. A polymer above its T_g acts as a tough ductile material, while below it the material is hard and glassy. On cooling, the T_g is sometimes known as the freeze temperature. The T_g is measured using dynamic mechanical thermal analysis (DMTA) or DSC. Typical temperature curves for shear modulus and mechanical loss factor, measured using a torsion pendulum, for different grades of PE are shown in Figure 3.5.

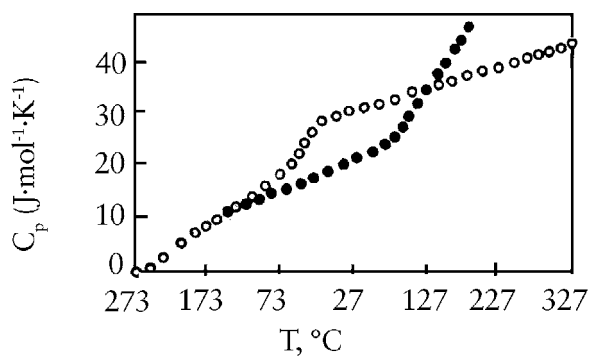


Figure 3.3 Specific heat *versus* temperature for amorphous (O) and crystalline (●) PE [23]

Drawn from the data in Handbook of Polyolefins: Synthesis and Properties, 1st Edition, Eds., C. Vasile and R.B. Seymour, Marcel Dekker, New York, NY, USA, 1993. Copyright Marcel Dekker, 1993.

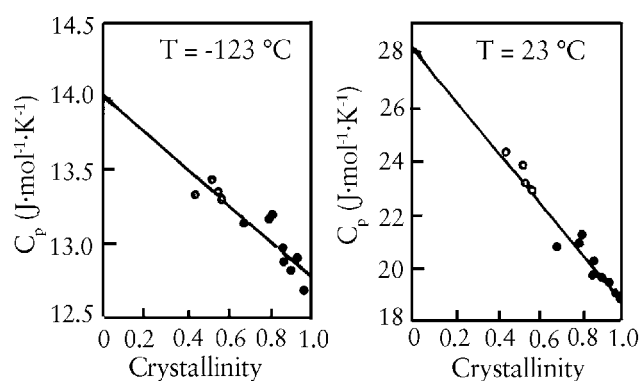


Figure 3.4 Specific heat of branched (O) and linear (●) PE as a function of crystallinity at various temperatures [23]

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Table 3.6 Heat capacity at constant pressure c_p (J/(mol K)) for amorphous and crystalline PE		
Temperature (°C)	Amorphous PE	Crystalline PE
-123	14.06	12.83
-73	18.92	15.57
-23	28.25	18.55
27	30.89	21.81
77	33.06	25.25
127	35.22	34.19
177	37.38	44.98
227	39.54	–
277	41.71	–
327	43.87	–

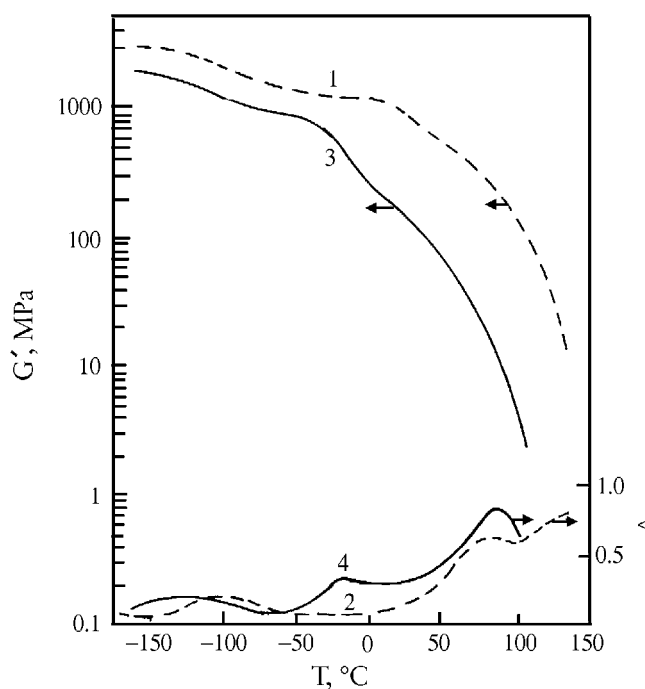


Figure 3.5 Typical DMTA curves for PE showing different transition temperatures. Curves 1, 2: one CH_3 per 1000 carbons, density 0.960 g/cm^3 ; Curves 3, 4: thirty CH_3 per 1000 carbons, density 0.918 g/cm^3 [23]

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The main features of the temperature dependence of the loss factor ($\tan \delta$) for LDPE and HDPE are presented schematically in **Figure 3.6**. The curve for LDPE shows clearly resolved α , β , and γ loss peaks. For HDPE, the low-temperature γ peak is very similar to that of LDPE, but the β relaxation is hardly resolved and the α relaxation is often considerably modified, appearing to consist of at least two processes (α and α') with different activation energies. The high-temperature behaviour is also dependent on whether loss angle or loss modulus is the quantity being measured. The α , β , and γ relaxations occur in all forms of PE. As regards the origin of these relaxations, the mechanical strengths of all three relaxations relate to the amorphous fraction, and both mechanical and dielectric measurements show that the location of the α relaxation depends on the crystal lamellar thickness. The activation energies for α and β relaxations in HDPE and LDPE are given in **Table 3.7**.

PE has the following transition/relaxation temperatures (**Table 3.8**). The α relaxation is observed between 20 and $60 \text{ }^\circ\text{C}$. The intensity of the α relaxation increases with increasing density of PE but then levels off at higher densities. The α peak is very sensitive to thermal history and is ascribed to the crystalline phase. The pre-melting or intra-crystalline process is designated as the α_c transition lying at about $0.87T_m - 0.9T_m$. There is also an amorphous inter-crystalline process (α_a) lying just below the α_c relaxation. T_{LL} is a liquid-liquid amorphous phase relaxation. The α_c peak should be strongest when the crystallinity of PE increases, while the α_a and T_{LL} amorphous phase events should be strongest in branched PE. During α_c relaxation the chains in interior crystals are mobile, e.g., chain rotation, translation, and twist. The α_a relaxation has been designed as a viscoelastic process due to the motion of the chain folds, loops, and molecules at the crystal surfaces.

The β relaxation occurs between -35 and $-5 \text{ }^\circ\text{C}$ depending on the type of PE, its intensity being high for LDPE and very low for HDPE. It is due to the motion of branches in the amorphous matrix. The β relaxation can be explained in terms of the glass transition temperature T_g . The greater the

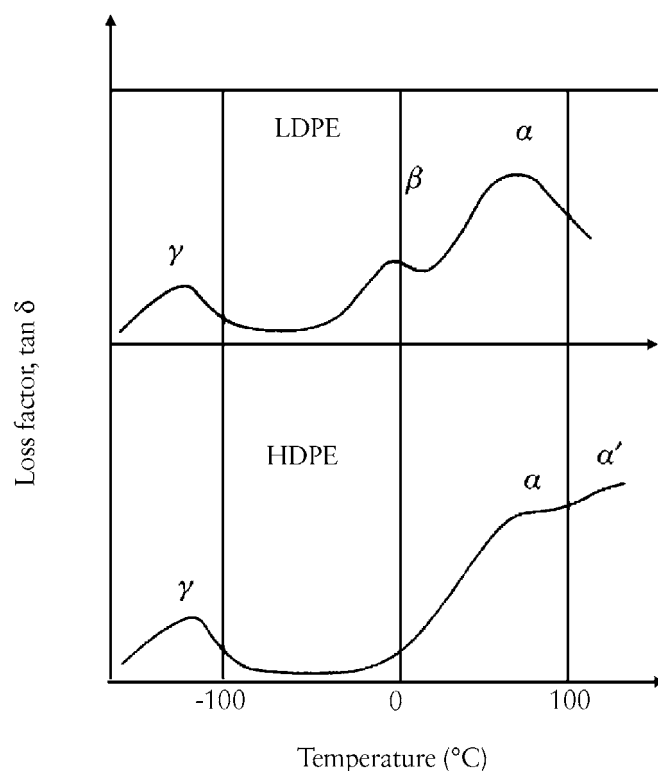


Figure 3.6 Schematic diagram showing α , α' , β , and γ relaxation processes in LDPE and HDPE [29]

Sample	β relaxation activation energy (kJ/mol)	α relaxation activation energy (kJ/mol)
Isotropic LDPE	430	120
Oriented LDPE	500	110
Isotropic HDPE	Not present	120
Oriented HDPE	Not present	80–90

α relaxation		β relaxation		γ relaxation	
ν (Hz)	T (°C)	ν (Hz)	T (°C)	ν (Hz)	T (°C)
LDPE (branched)					
0.3	67	0.3	-5	1.25	-133
1.2	54	4.1	-5	8.6	-107
39	60	150	-20	324	-115
150	82	540	-8	1.2×10^3	-108
200	87	520	7	1.15×10^3	-108
600	112	6000	47	1.9×10^4	-73
4×10^4	≥ 87	4×10^4	2	4×10^4	-93
1×10^5	≥ 47	1×10^5	12	1×10^5	-73
2×10^6	87	2×10^6	27	2×10^6	-63
HDPE					
0.3	100			1.25	-120
0.2	95	8	0	10	-100
<460	≥ 107	1×10^3		1.57×10^3	-100
3000	147		22	1.63×10^3	-96

amorphous fraction, the more intense is the β relaxation. The thermal expansion, specific heat, and dynamic mechanical loss data indicate the presence of two relaxation temperatures for LDPE, HDPE, bulk crystallisation PE, and several other polymers (including PP). The lower temperature is denoted as $T_g(L)$, which appears identical to the conventional T_g at zero crystallinity. The higher temperature is denoted as $T_g(U)$ and becomes detectable as the crystallinity increases (Figure 3.7).

The γ relaxation for HDPE occurs at -170°C and at 111 and -114°C for linear and branched LDPE, respectively. Its intensity decreases with increasing density. The γ relaxation is caused by small, local, short-range segmental motion of amorphous PE, involving three or four methylene groups, or could be due to the defects in the crystalline phase.

In many cases, the T_g value of PE is considered as -21°C . Actual values may be observed between -120 and -20°C depending on the frequency/heating rate. In the case of copolymers, T_g is strongly dependent on comonomer content. For example, ethylene–vinyl acetate (EVA) copolymers with $\sim 50\%$ VA content exhibit T_g values of -109°C , while for a VA content of $10\text{--}20\%$, T_g has values between -32 and -10°C . The Vicat softening point (see Section 3.4.5 for definition) is 95°C for LDPE and 120°C for HDPE.

The crystalline melting point varies between 138 and 120°C for linear PE and for a PE with 8.7 branches per 100 carbon atoms, respectively, depending on the grade (branching), frequency/heating rate, and molecular weight (Figure 3.8). Melting temperature of copolymers decreases with increasing comonomer content (or number of branches). PE copolymers (linear LDPE) and branch-containing polymers (due to lower crystallinity) and metallocene-catalysed PE have lower melting points compared to HDPE homopolymer.

Some properties of various grades of PE are given in Table 3.1. The properties of selected copolymers are summarised in Table 3.9.

3.4.4 Maximum Continuous Use Temperature

Maximum continuous use temperatures are based upon the Underwriter's Laboratories rating for long-term ($100,000$ hours) continuous use, and specifically on the elevated temperature that causes

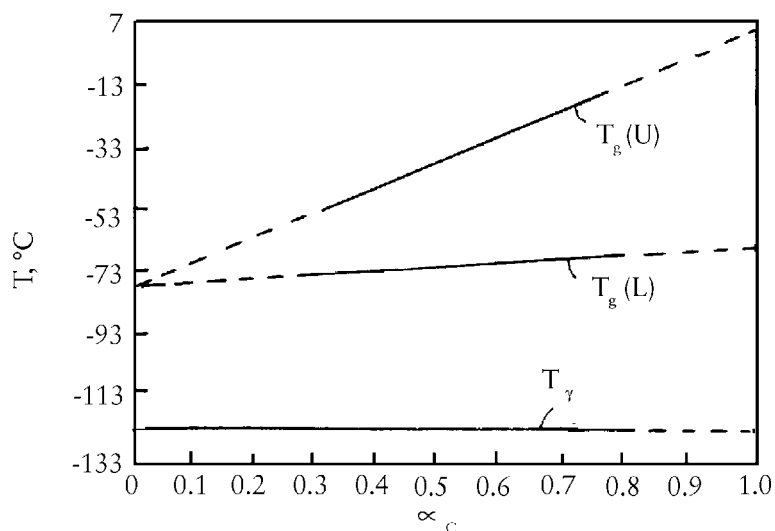


Figure 3.7 Schematic representation of the three amorphous transitions in bulk crystallised, semi-crystalline PE and their dependence on crystallinity. $T_g(U)$: the upper glass transition; $T_g(L)$: the lower glass transition; T_γ , the local mode (crankshaft process) [23]

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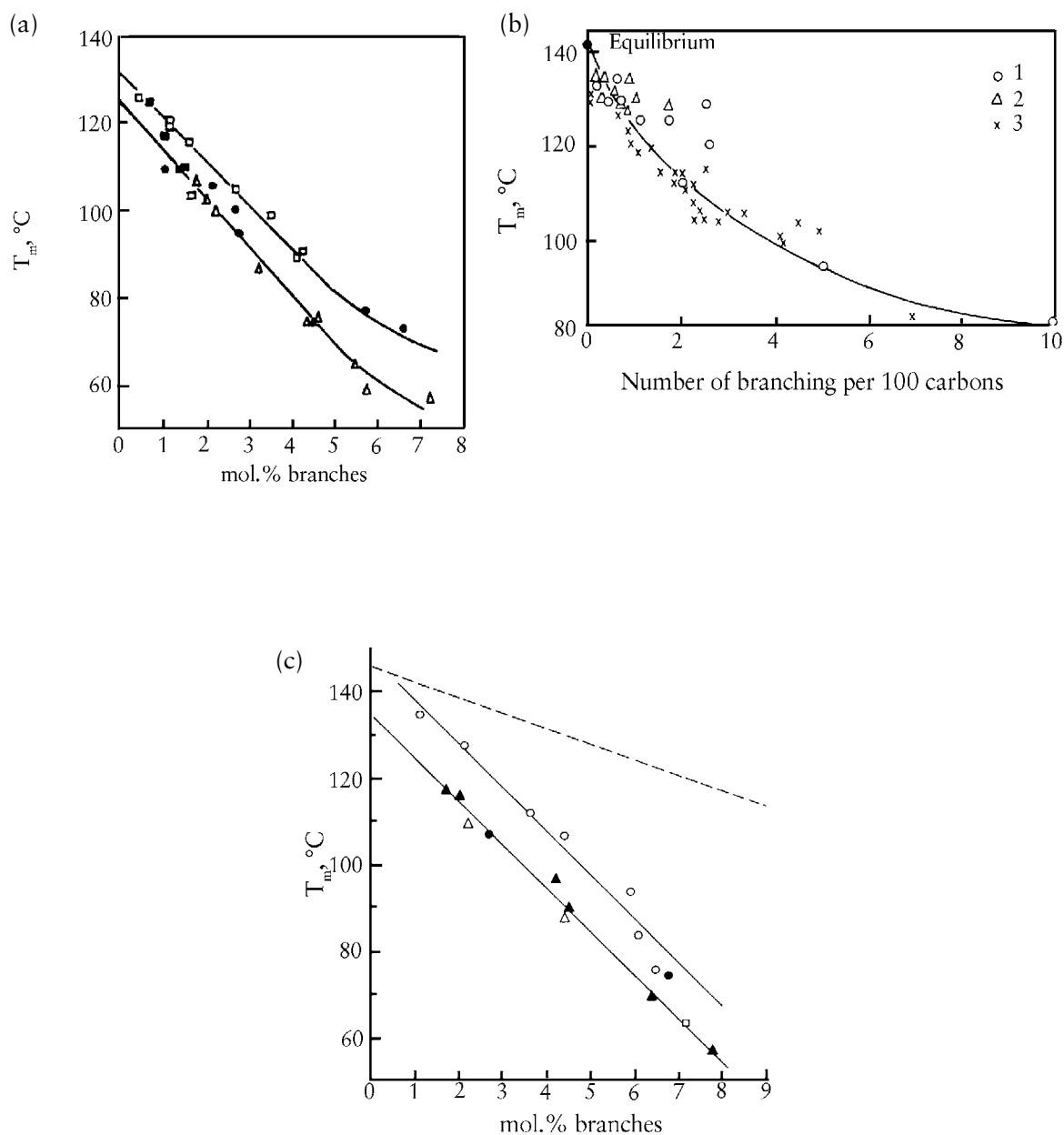


Figure 3.8 (a) Melting temperature (T_m) of rapidly crystallised fractions of PE-based copolymers as determined by DSC. Δ : hydrogenated polybutadiene with ethyl groups; \bullet : ethylene–vinyl acetate copolymer; \blacktriangle : diazoalkane copolymer with propyl side groups; \times : ethylene–1-butene copolymer; \blacksquare : ethylene–1-octene copolymer. (b) Melting temperature (T_m) of branched LDPE. 1: ethylene–propylene copolymer; 2: ethylene–1-butene copolymer; 3: branched PE [23]

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(c) Dilatometric-determined melting temperature of ethylene copolymers *versus* mole percent of branches. The dashed line represents equilibrium temperature for random copolymers. Experimental results: diazoalkane copolymers with methyl branch (O); ethyl branch (\square); propyl branch (\blacktriangle); hydrogenated polybutadiene (Δ); EVA (\bullet) [30]

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Table 3.9 Properties of ethylene copolymers and modified PE				
ASTM or UL test	Property	CPE	EP copolymer	EVA copolymers (12–33% VA)
Physical				
D792 [1]	Density (g/cm ³)		0.86–0.99	
	Max. operating temperature (°C)	60	60	50
	Mould temperature range (°C)	20–40	20–50	20–40; 20–40; 20–40
D570 [2]	Water absorption, 24 h (%)	0.01	0.01	0.05; 0.1; 0.13
Mechanical				
D638 [3]	Tensile strength (MPa)	12.5	26	19; 17; 10
D638	Tensile modulus (MPa)			
D638	Tensile elongation at yield (%)			
D790 [4]	Flexural strength (MPa)			
D790	Flexural modulus (GPa)	0.002	0.6	0.07; 0.02; 0.007
	Elongation at break (%)	700	500	750; 750; 900
	Strain at yield (%)	N/Y	N/Y	
D695 [5]	Compressive strength (MPa)			
D695	Compressive modulus (MPa)			
D785 [6]	Hardness (Shore D)			
D256 [8]	Izod notched impact (kJ/m)	>1.06	0.15	>1.06; >1.06; >1.06
	Mould shrinkage (%)	3	1.5	2; 2; 2
	Surface hardness	SA70	RR75	
Thermal				
D696 [9]	Coefficient of linear thermal expansion (10 ⁻⁵ m/m/°C)	18	16–25	18; 18; 18
	Heat capacity (J/g/K)		2.22	
	Brittle point (°C)		–55 to –65	
	Glass transition temperature (°C)		–55	
D648 [10]	Heat deflection temperature at 0.45 MPa and 1.80 MPa (°C)	35 and 25	93 and 54	20
D3418 [11]	Melt temperature (°C)	66–77	93–110	71–104; 60–93; 54–88
C177 [12]	Thermal conductivity (BTU in/ft ² /h/°F (10 ⁻⁴ cal/cm/s/°C) or kW/m/K)		1757	
UL94 [13]	Flammability	HB	HB	HB; HB; HB
	Oxygen index (%)	22	17	19; 19; 20
Electrical				
D149 [14]	Dielectric strength (MV/m)	12	30	30; 27; 25
D150 [15]	Dielectric constant at 1 kHz	5.5	2.3	2.65; 2.9; 3.1
D150	Dissipation factor at 1 kHz	0.1	5.6666 × 10 ⁻⁴	0.015; 0.02; 0.03
D257 [16]	Volume resistivity at 50% RH (Ω cm)	13	15	16
<p>CPE: chlorinated PE EP: ethylene-propylene HB: horizontal burn RH: relative humidity</p>				

the ambient temperature tensile strength of the material to fall to half its unexposed initial value following exposure to that elevated temperature for 100,000 hours. The test provides a continuous use temperature for a plastic in the absence of stresses. This temperature is 55 °C for HDPE and 50 °C for LDPE, quite low temperatures. Occasionally it is required that the service life of a component is predicted at a temperature above its continuous use temperature or *vice versa*. As a rule of thumb, a 10 °C increase in temperature is equivalent to a decade increase in time. However, the maximum use temperature of a polymer depends on the specific grade and its heat stabilisation system, and should be carefully noted from the relevant trade literature. The functionality of the polymer for high-temperature application might be quite limited in the presence of stresses.

3.4.5 Heat Deflection Temperatures and Softening Points

The heat deflection temperature (HDT) is defined as the temperature at which a standard test bar deflects by a standard amount under a standard load. Generally, loads of 0.45 and 1.8 MPa are used. It may be used to distinguish between those materials that are able to sustain light loads at high temperatures. The HDT of a specimen is affected by the presence of residual stresses. Warpage of the specimen due to stress relaxation may lead to erroneous results. Injection moulded specimens tend to give a lower HDT than compression moulded specimens. This is because the latter are relatively stress free. The HDT of PE (Table 3.1) is lower than that of PP (88–95 °C) and than those of other plastics (e.g., HDT of polycarbonate is 143 °C).

The Vicat softening temperature is the temperature at which a flat-ended needle of 1 mm² circular cross-sectional area will penetrate a thermoplastic specimen to a depth of 1 mm under a specified load using a selected uniform rate of temperature rise. Above the softening point, the material becomes progressively softer. The practical application of the Vicat softening point data is limited to quality control and material characterisation. It is taken as a rough estimate of the maximum temperature for ejection of an article from an injection moulding machine. The Vicat softening point of PE is 85–100 °C for LDPE and 112–132 °C for HDPE.

The data obtained from these tests cannot be used to predict the behaviour of plastic materials at elevated temperature, and cannot be used in designing a part or selecting and specifying a material. If an article is subjected to high temperature in the absence of stresses, the maximum continuous use temperature (Section 3.4.4) can provide a suitable criterion for material selection. In addition, if load-bearing properties are required from a component at high temperatures, the modulus of the plastic as a function of temperature could provide data for the design calculations.

The difference between the flexural modulus–temperature curves of different plastics is explained on the basis of amorphous and semi-crystalline structure. Amorphous polymers maintain their strength quite well up to their maximum use temperature. Their strength falls sharply when their T_g is reached. Semi-crystalline polymers, such as PE and PP, slowly lose their strength above their T_g . The residual strength of a semi-crystalline material may be higher than that of the amorphous material at a higher temperature, and an amorphous polymer may be stronger at a lower temperature.

3.4.6 Brittleness and Brittle Temperature

A material for which fracture is accompanied by a large irreversible deformation is called tough. A brittle fracture is defined as that in which there is relatively little permanent plastic flow. Among the fundamental properties of PE, the crystalline texture has a pronounced influence on the ductile–brittle transition, and the effects of thermal history can also be very large. An increase in the density of PE will increase brittleness, so much so that the slow increase in density on storage of PE articles can be accompanied by dramatic changes in impact behaviour, particularly pronounced in more highly crystalline polymers. There is a reduction in the tendency to brittle fracture as the molecular weight of PE increases. A narrow MWD has been reported to promote toughness and impact resistance in HDPE. Extremely ‘tough’ PE is UHMWPE with a M_w of 1.5×10^6 .

Brittle temperature is very closely related to the T_g and determines the minimum temperature at which a semi-crystalline polymer could be used without significant loss of its impact properties. According to ASTM D746 [31], the brittle temperature of LDPE is $-156\text{ }^\circ\text{C}$ and that of HDPE lies between -156 and $-73\text{ }^\circ\text{C}$ (brittleness temperature for HDPE is $-70\text{ }^\circ\text{C}$), which explains the good performance at low temperatures.

At low temperatures, all plastics tend to become rigid and brittle, because the mobility of chains is greatly reduced. Impact strength at lower temperatures, e.g., $-40\text{ }^\circ\text{C}$, can be considered as a useful criterion for material selection for use under arctic conditions. Brittle temperature is close related to T_g and is defined as the temperature at which 50% of specimens exhibit brittle failure under specified impact conditions. LDPE and HDPE have lower brittle temperature compared with other plastics [32].

3.4.7 Thermal Conductivity

The lower thermal conductivity of PE and other plastics compared to metals gives protection against external temperature changes and so PE can be used for insulation applications. Lower thermal conductivity limits the production cycles and can result in cooling strains in thick sections, which may lead to warpage of an article. The conductivity is a function of density and temperature (Figure 3.9). Foamed PE has lower conductivity than the unfoamed PE.

3.4.8 Thermal Expansion

The coefficient of thermal expansion is defined as the fractional change in length or volume of a material for a unit change in temperature. The coefficient of thermal expansion of plastics is

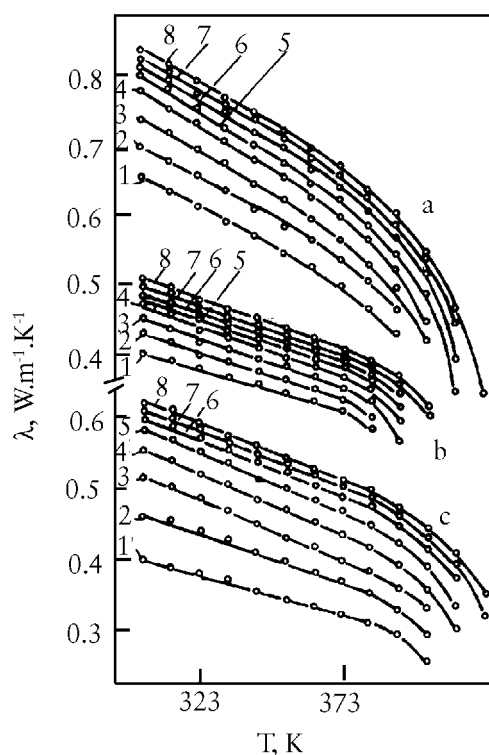


Figure 3.9 Dependence of the thermal conductivity on temperature for (a) LDPE, (b) HDPE, and (c) UHMWHDPE at various pressures. 1: 0.1 MPa; 2: 10 MPa; 3: 20 MPa; 4: 30 MPa; 5: 40 MPa; 6: 60 MPa; 7: 80 MPa; 8: 100 MPa [23]

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considerably higher than that of metals, up to six to ten times higher. This difference in the coefficient of thermal expansion can lead to internal stresses and stress concentrations, consequently, premature failure may occur. Thermal expansion gives significant volume changes on melting. A plastic can shrink by 1–2% in moulding, and this must be allowed for when designing a tool. Mould shrinkage and thermal expansion for PE are 3.0% and the thermal expansion coefficient varies between 12×10^{-5} and 20×10^{-5} m/m/°C. The use of fillers reduces the thermal expansion coefficient considerably and brings the value closer to that of metals and ceramics.

3.5 Mechanical Properties

The presence of a crystalline phase enables PE to retain its mechanical strength over a large temperature range, despite the relatively low T_g . Probably the most important and significant single mechanical measurement to be made on PE is the determination of elastic modulus or ‘stiffness’. The stiffness of PE increases linearly with density (Figure 3.10) and depends on temperature (Figure 3.11). It is evident from Figure 3.11 that the decrease in modulus of highly branched PE with increasing temperature follows a curve quite different from that of more dense linear polymers.

Yield strength, tensile strength, and elongation at break are mechanical properties that are particularly important in terms of practical applications. They represent the maximum elastic strength, the ultimate strength, and the amount that the PE can be drawn, respectively. These are commonly determined from stress–strain curves (Figure 3.12).

The tensile strength decreases with increasing temperature. Increasing density causes an increase in tensile strength, as does an increase in molecular weight. Impact strength can be defined as the amount of energy that the PE can take up before some permanent damage is done. The area under the stress–strain curve, i.e., approximately the product of tensile strength and elongation, can be somewhat arbitrarily taken as the ‘impact strength’. The impact strength increases rapidly with molecular weight. As for temperature, elongation and tensile strength act oppositely, so that a

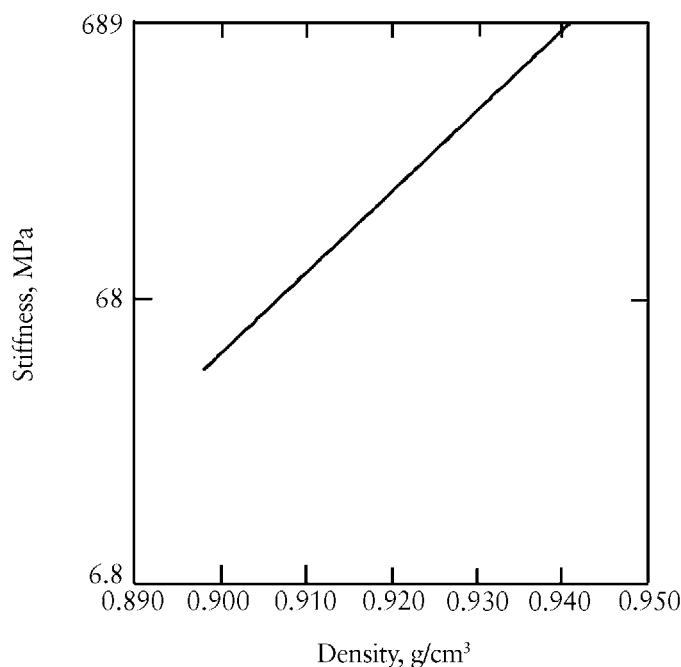


Figure 3.10 Effect of density on the stiffness (elastic modulus) of PE [33]

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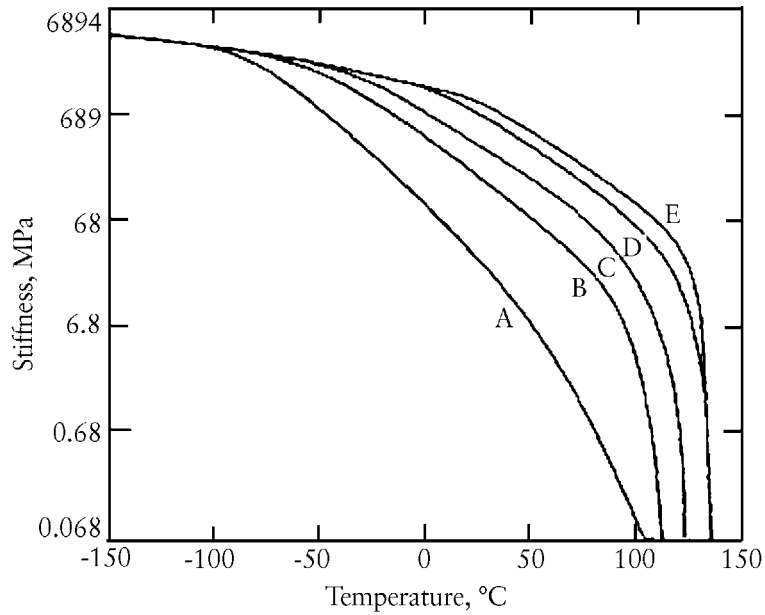


Figure 3.11 Effect of temperature on the stiffness of PE of various densities. A: 0.895 g/cm³; B: 0.918 g/cm³; C: 0.935 g/cm³; D: 0.950 g/cm³; E: 0.968 g/cm³ [33]

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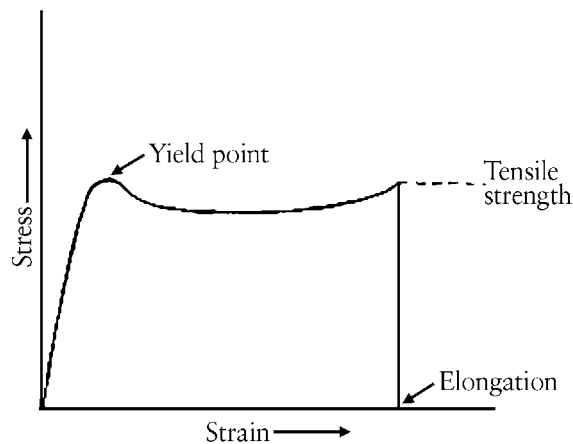


Figure 3.12 Idealised stress–strain curve for a typical crystalline olefin polymer [33]

maximum in impact strength can be expected in a particular temperature range. At normal rates of loading, impact strength decreases with increasing density; at very low rates of strain, however, high-density polymers may have considerable impact strength.

3.5.1 Short-term Mechanical Properties: Static Mechanical Properties

It is well known that, for a stress–strain curve typical of a ductile plastic, tensile force increases with increasing elongation, up to the yield point. After this, the force initially decreases, i.e., the material can be further stretched with a smaller force. This is accompanied by a marked necking of the

cross-section of the test specimen. When this necking down has progressed along the entire length of the specimen, the force increases again until elongation at break is reached. The second increase in deformation resistance is due to partial orientation of the macromolecules, which strengthens the material (Figure 3.13). The flexural modulus and tensile strength of PE are the lowest of all plastics, those of HDPE being close to those of PP.

The short-term stress–strain data for a plastic are of limited use and should only be used for pre-selection of material. In reality, plastic components are seldom designed for and subjected to such high levels of strain as applied in short-term tests. The product failure is brittle in nature. The long-term creep and fatigue properties are more important for structural applications.

3.5.1.1 Effect of Test Speed

As for other viscoelastic thermoplastics, increasing the speed of the test decreases the observed flexibility and increases the observed brittleness.

3.5.1.2 Effect of Temperature

Both tensile strength and elongation at break depend on temperature: the former decreases and the latter increases with temperature (Figure 3.14). The stiffness (hardness) of PE is a function of temperature (Figure 3.15). The variation of flexural modulus of different grades of PE as a function of temperature is shown in Figure 3.11.

Homopolymers are slightly stiffer than copolymers at room temperature. However, the difference between the two types decreases as the temperature increases.

PE becomes more ductile as the usage temperature increases, shown by an increase in elongation at break and a decrease in ultimate tensile strength and yield stress.

3.5.1.3 Effect of Draw Ratio

The tensile modulus increases with the draw ratio (Figure 3.16). An anisotropy in mechanical properties is created.

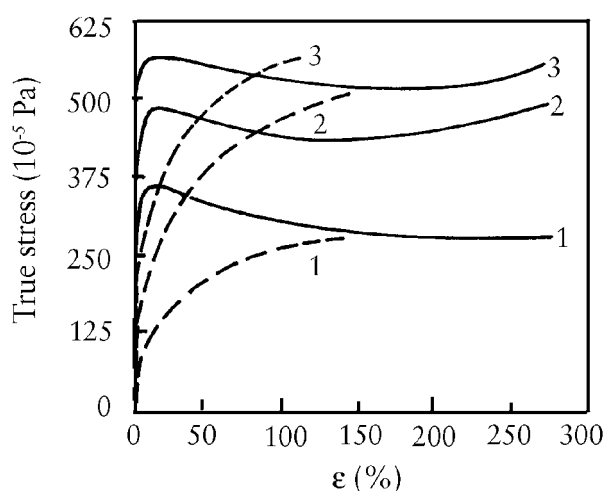


Figure 3.13 True tensile stress–strain curves for HDPE (solid lines) and LDPE (dashed lines) at various pressures. 1: 1 kg/cm²; 2: 1000 kg/cm²; 3: 2000 kg/cm² [23]

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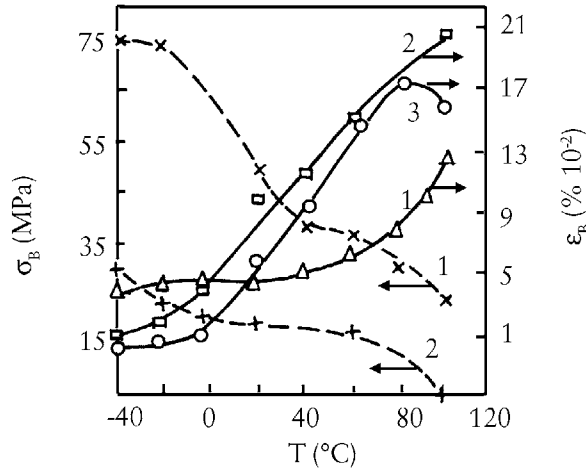


Figure 3.14 Dependence of tensile strength (σ_B) and elongation at break (ϵ_B) on temperature for PE specimens. 1: UHMWHDPE, $\bar{M}_w = 1,500,000$, $\rho = 0.937 \text{ g/cm}^3$; 2: HDPE, $\bar{M}_w = 260,000$, $\rho = 0.950 \text{ g/cm}^3$; 3: LDPE, $\bar{M}_w = 190,000$, $\rho = 0.952 \text{ g/cm}^3$ [23]

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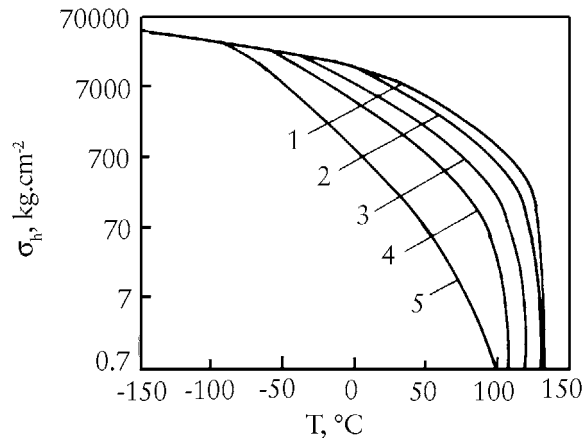


Figure 3.15 Dependence of hardness on temperature for PE of various densities. 1: 0.968 g/cm^3 ; 2: 0.950 g/cm^3 ; 3: 0.935 g/cm^3 ; 4: 0.918 g/cm^3 ; 5: 0.895 g/cm^3 [23]

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For a highly oriented sample, a plot of Young's modulus against the angle of the draw direction shows the lowest stiffness at an angle close to 45° to that direction (Figure 3.17).

Time-temperature equivalence, in its simplest form, implies that the viscoelastic behaviour at one temperature can be related to that at another temperature by a change in the timescale only. The compliances at temperatures T_1 and T_2 can be superimposed exactly by a horizontal displacement $\log a_T$, where a_T is called the shift factor (Figure 3.18(a)). Similarly, for dynamic mechanical experiments, double logarithmic plots of $\tan \delta$ versus frequency show an equivalent shift with the

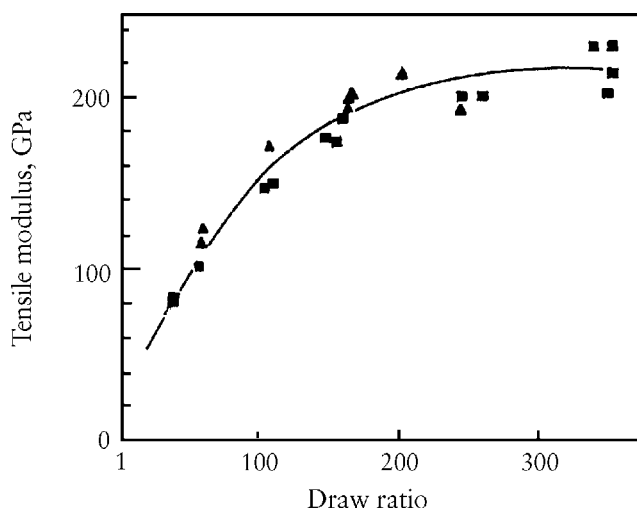


Figure 3.16 Variation of the tensile modulus with drawn ratio for super-drawn PE crystalline morphologies of different molecular weight grown from solution: $\bar{M}_w = 21 \times 10^5$ (■), 15×10^5 (▲) [23]

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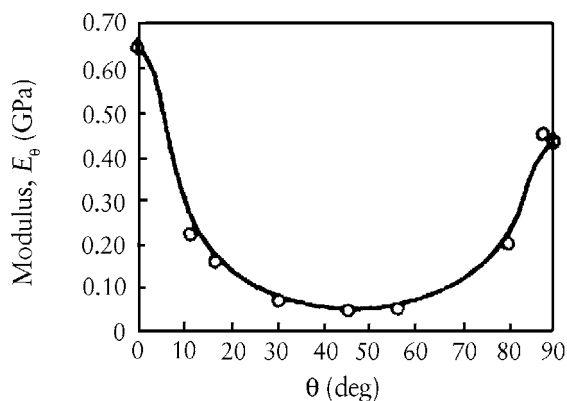


Figure 3.17 Variation of Young's modulus with angle θ to draw direction for LDPE sheet drawn to a draw ratio of 4.65 [29]

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temperature (**Figure 3.18(b)**). A series of creep compliances each typically extended over 2 hours so that individual tests can be performed on successive days, can be plotted using a specimen that has been mechanically conditioned at the highest temperature needed. The individual plots are then transposed along the logarithmic time axis until they coincide, using any required temperature within the experimental range as the reference value (**Figure 3.19**).

The mechanical properties of PE are strongly dependent on time, temperature, the level and type of applied stress, and the test speed. The apparent stiffness or elastic modulus of all plastics

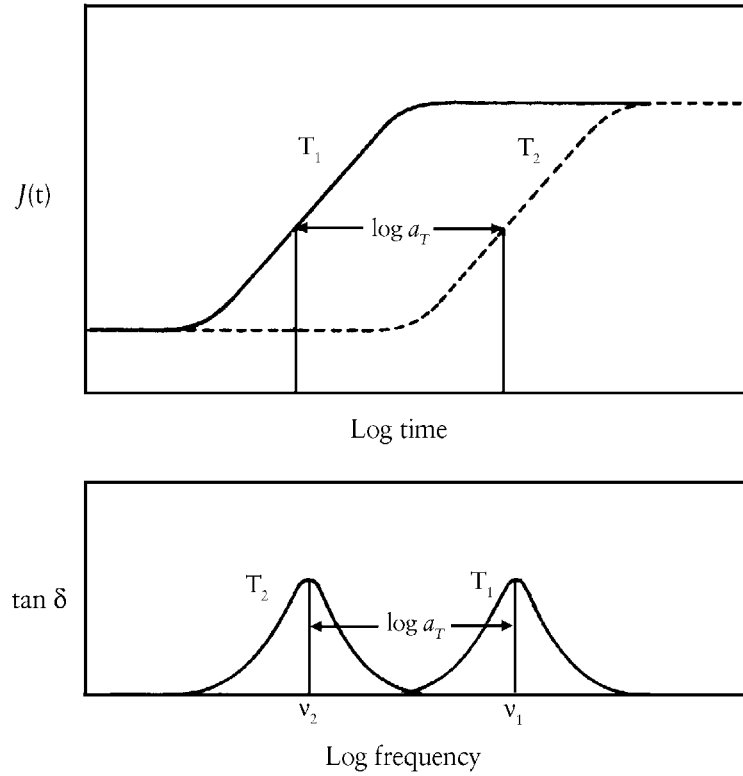


Figure 3.18 Schematic diagrams illustrating the simplest form of time–temperature equivalence for (a) compliance, $J(t)$, and (b) loss factor, $\tan \delta$ [29]

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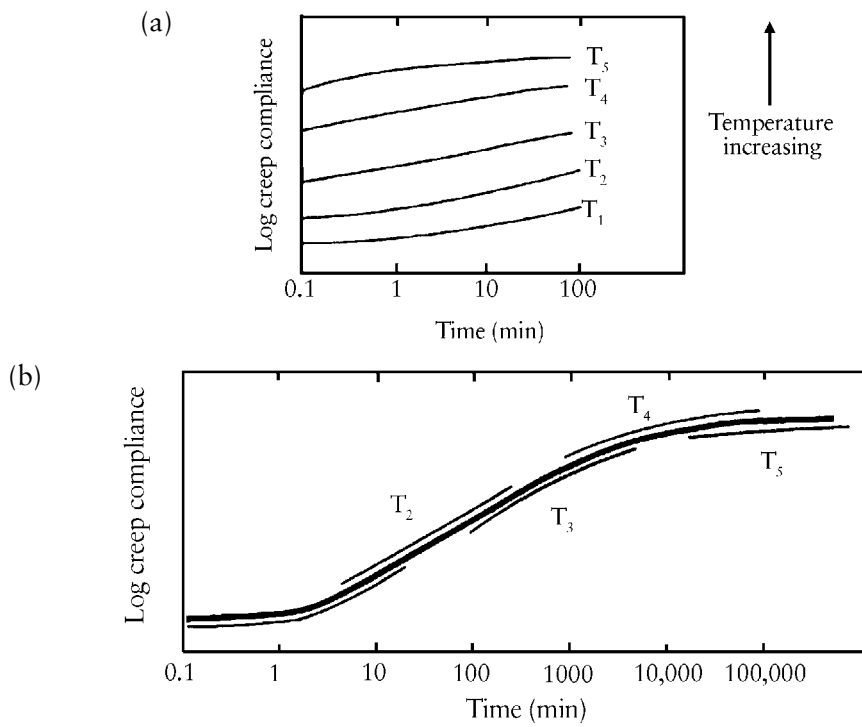


Figure 3.19 (a) Schematic plots of creep at different temperatures. (b) Master curve of creep from superposing the plots of (a) [29]

Adapted from I.M. Ward and J. Sweeney, An Introduction to the Mechanical Properties of Solid Polymers, Wiley, Chichester, UK, 2004. Copyright Wiley, 2004.

decreases with time under load, due to the process of stress relaxation and creep. Similarly, the modulus decreases with increasing temperature. Therefore the effect of time and temperature on the mechanical properties is interchangeable. The Williams–Landel–Ferry (WLF) theory and other theories describe these phenomena at the molecular level [34]. The effect of time during service can be simulated in the short term using high temperature. This superposition of the time and temperature can be used in practice to predict the durability of products.

3.5.1.5 Impact Strength

In Izod and Charpy tests a notch is incorporated in the sample to concentrate stress, which normally leads to brittle failure. The impact strength is reduced as the notch gets sharper. Consequently, sharp corners in load-bearing sections must be avoided in the design of an article as a general rule for all plastics. The impact strength of an article depends on the inherent molecular structure of the grade used and the morphology arising from the processing conditions. Changes in the geometry of an item can have a major effect on its toughness rating. Impact strength increases with temperature up to ~40 °C, and then decreases (Figure 3.20). Impact strength also increases with molecular weight and, more markedly, with comonomer content.

Notched: PE copolymers have higher impact strength than homopolymers. For example, the impact strength of EP copolymers is about 16 J/12.7 mm and EVA copolymers do not break under these conditions.

Falling dart impact test (ASTM D1709 [35]): The failing weight or dart drop test method simulates actual day-to-day use and can be carried out either on standard laboratory specimens or on the articles themselves. Failure may occur in various ways, ranging from brittle to ductile failure. Brittle fracture must be avoided by the proper selection of polymer grade. A significant reduction in the dart impact strength as well as the tear strength with increasing long-chain branching (LCB) is observed for various PE. The dart impact varies between 60 and 150 g and the tear strength is about 24–44 g. An increase in the LCB level results in lower impact strength and transverse direction tear strength of blown films.

Tensile impact strength: Impact strength tests permit no differentiation between specimens undergoing the test without failure. In this respect, the tensile impact strength test is superior, because other variables are eliminated (notch sensitivity, loss factor, and specimen thickness). It can be used

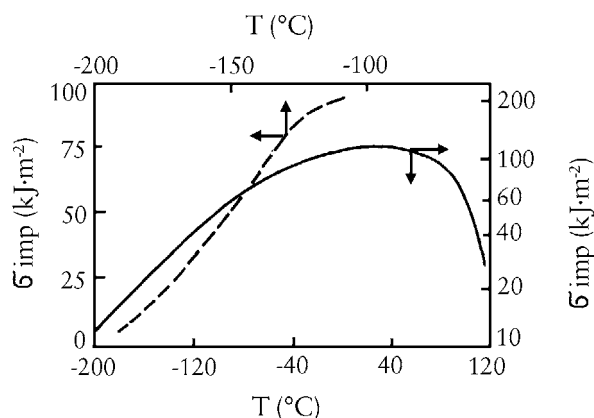


Figure 3.20 Dependence of the impact strength (DIN EN ISO 179-1 [36]) of UHMWPE on temperature: without notch (dashed line); with sharp (15°) notch (solid line) [23]

Redrawn from Handbook of Polyolefins: Synthesis and Properties, 1st Edition, Eds., C. Vasile and R.B. Seymour, Marcel Dekker, New York, NY, USA, 1993. Copyright Marcel Dekker, 1993.

for very thin specimens. The tensile impact test consists of a specimen-in-head type of set-up. The specimen is mounted on a pendulum and attains full kinetic energy at the point of impact. One end of the specimen is mounted on the pendulum and the other end is gripped by a crashing member that travels with the pendulum until the instant of impact. The energy of break by impact in tension is determined by the kinetic energy extracted from the pendulum in the process of breaking the specimen. Tensile impact strength testing of PE measured according to ASTM D1822 [37] method gives values for LDPE of 378 kJ/m² and for MDPE and HDPE of 126 kJ/m².

3.5.1.6 Creep

Creep is the time-dependent change in strain following a step change in stress. Creep in polymers at low strains (1%) is essentially recoverable after unloading, without the need for annealing at a raised temperature. The maximum insight into the nature of creep is obtained by plotting the logarithm of creep compliance against the logarithm of time over a very wide timescale [29].

Like other viscoelastic materials, PE exhibits creep (or cold flow). Creep is the deformation (or total strain) that occurs after a stress has been applied. Its extent depends on the magnitude and nature of the stress, the temperature, and the time for which the stress is applied. Over a period of time, PE undergoes deformation even at room temperature and under relatively low stress. After the removal of stress, a moulding more or less regains its original shape, depending on the time under stress and magnitude of the stress. Recoverable deformation is known as elastic deformation and permanent deformation as plastic deformation.

Typical creep curves plot deformation or creep against time on a logarithmic scale for a range of loads or stresses. This basic creep data can be used to plot isochronous stress–strain curves, isometric stress curves, or creep modulus as a function of time. In an isochronous graph, stress is plotted against strain at a constant series of time intervals. In an isometric graph, stress or strain is plotted as a function of time for a series of constant strains or stresses. Creep modulus curves show the time-dependent value of modulus [32]. As the properties of polymers are a function of temperature, these curves can be produced at different temperatures. These types of data are available from raw material suppliers in most cases. However, sometimes the creep data for the conditions to which a component might be subjected in service are not available. Hence the data are extrapolated to the required conditions. Care should be exercised in extrapolating the data to higher temperatures or longer duration outside the experimental creep data range.

Copolymer type and MFR also influence the creep behaviour. HDPE has a similar modulus to PP. At an equivalent time under similar load, the creep modulus of HDPE is less than that of PP. The creep resistance of amorphous plastics is much better than that of semi-crystalline plastics such as PE and PP. The creep resistance of PE can be improved by the addition of fillers or reinforcements. The creep behaviour of moulded articles is affected by the residual stress or orientation effect in the moulded article.

Young's modulus as a function of draw ratio is shown in **Figure 3.21**. It can be seen that the modulus, which even at room temperature can reach an appreciable fraction of the crystal modulus, depends only on the final draw ratio and is independent of the relative molecular mass and the initial morphology. Hence an appropriate model appears to be one that depends on the structure produced during deformation rather than on the starting material.

Wilding and Ward [38] used the Eyring rate process to model the creep of ultra high-modulus PE and showed that at high strains, which correspond to long creep times, the creep rate reaches a constant value called the plateau (or equilibrium) creep rate (**Figure 3.22**). For polymers of low relative molecular mass, the stress and temperature dependence of the final creep rate can be modelled by a single activated process with an activation volume of 0.08 nm³. For polymers of higher molecular mass, and for copolymers, the permanent flow process is activated only at high stress levels, which suggests that there are two Eyring processes coupled in parallel.

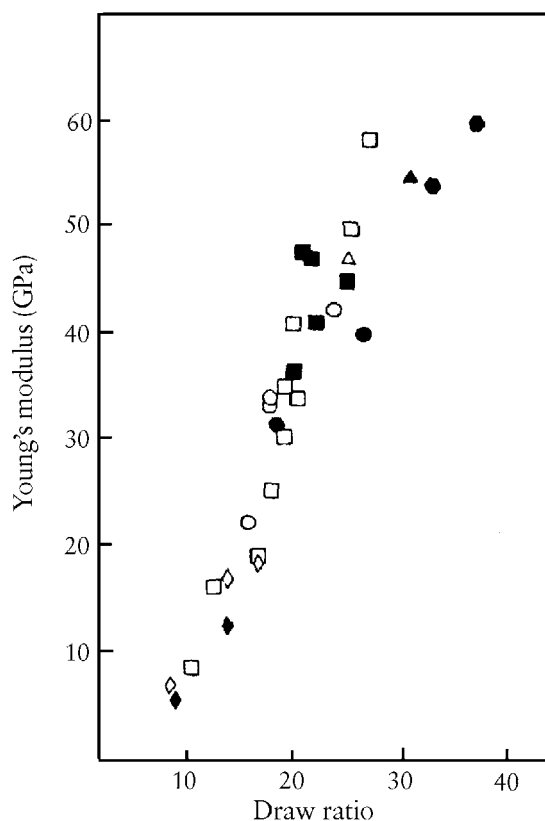


Figure 3.21 Ten second isochronal creep modulus, measured at room temperature, as a function of draw ratio for a range of quenched (open symbols) and slowly cooled (filled symbols) samples of linear PE drawn at 75 °C: Rigidex 140-60 (*), Rigidex 25 (Δ , \blacktriangle), Rigidex 50 (\square , \blacksquare), P40 (O, \bullet), H020-54P (\diamond , \blacklozenge) [29]

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3.5.1.7 Fatigue or Stress Relaxation

In this case a material is subjected to constant strain, and the relaxation in the stress is measured as a function of time. This scenario occurs in press fits, springs, screws, washers, and so on, which undergo stress relaxation during service.

3.5.2 Dynamic Fatigue

Materials subjected to cyclic loads or stresses fail at a point far below the ultimate strength measured in short-term mechanical tests. The cyclic loads may be caused by periodic or intermittent loading in on/off situations. It is well known that amorphous plastics are more susceptible to fatigue than semi-crystalline plastics such as PE. However, it should be noted that semi-crystalline materials also suffer from dynamic fatigue and the stress level decreases significantly as the number of cycles increases, although semi-crystalline materials do not undergo the ductile to brittle transition of amorphous materials. Fatigue data are usually published in the form of Wohler curves, where stress or strain amplitude is plotted against the number of cycles to failure on a logarithmic scale. The stress levels for cycles to failure for different materials, including PE, are compared in **Figure 3.23**.

Fatigue strength is sensitive to stress concentration such as that caused by notches or sharp corners. It depends on the stress frequency – its effect at low frequencies is much more severe, and therefore failure can occur earlier than that predicted using high-frequency tests. The number of cycles to failure decreases with increasing temperature.

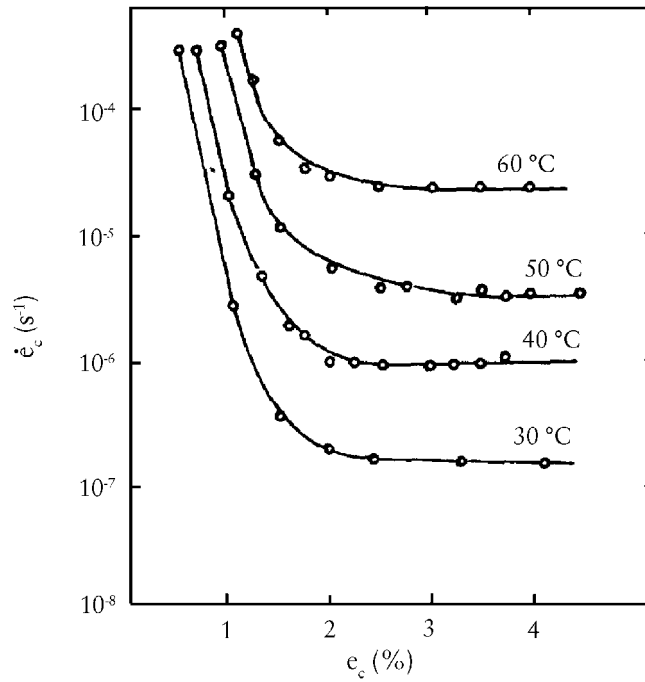


Figure 3.22 Sherby–Dorn plots of creep for ultra high-modulus PE at different temperatures [29]
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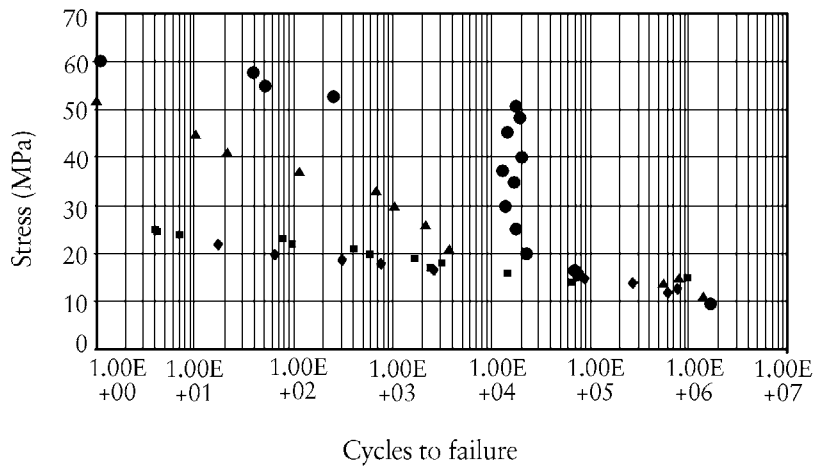


Figure 3.23 Stress levels for cycles to failure for different plastics: polycarbonate (●), PP (■), acrylonitrile-butadiene-styrene (ABS) (▲), HDPE (◆) [32]

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3.5.3 Mechanical Properties of Filled Grades

The properties of filled or reinforced grades of PE are strongly influenced by the type and the amount of filler (Tables 3.10 and 3.11). For example, the density of a heavily filled grade can be up to 50% higher than that of the unfilled material.

Table 3.10 Properties of various filled PE grades

Grade	Density (kg/m ³)	Modulus (MPa)	Elongation at break (%)	Limit resistance (MPa) to		Impact strength (kJ/m ²)	Shore hardness
				Stretching	Bending		
UHMWHDPE	934		450	45		NB	40
HDPE	948-960	6200	200-800	23-25		NB	2-12
HDPE + 20% glass fibres	1100	6500	1.5	50	70		
HDPE + 30% glass fibres	1180	6210	1.9	86.2		239.9	69.3
HDPE + 33-37% calcite	1200		20.0	19.0		35.0	75
HDPE + 40-44% calcite	1400		10.0	19.0		20.0	
HDPE + 48-52% calcite	1400		6.0	18.0		14.0	
HDPE + 5% asbestos			23	25.6		42.4	5.9
HDPE + 10% asbestos			12	25.2		26.4	6.0
HDPE + 15% asbestos			5	25.0		21.3	6.75
HDPE + 30% asbestos			0	25.4		7.45	7.7
HDPE + 40% asbestos			0	26.3		13.23	7.2
Crosslinked HDPE	944			19.6			2.84
Crosslinked HDPE + 5% wood flour	951	20.8		20.8			3.81
Crosslinked HDPE + 20% wood flour	1008			26.2			4.19
Crosslinked HDPE + 30% wood flour	1032			23.0			6.60
LDPE	923		600	11.03			52
LDPE + 25% CaCO ₃	1065		200	11.13			55
LDPE + 75% CaCO ₃	1288		20	11.83			59
EVA (10% VA)	927		700	13.05			45
EVA (10% VA) + 25% CaCO ₃	1068		500	9.85			49
EVA (10% VA) + 50% CaCO ₃	1187		250	8.64			50
EVA (10% VA) + 75% CaCO ₃	1291		100	9.20			52
EVA (10% VA) + 100% CaCO ₃	1381		50	10.20			55

NB: no break

Table 3.11 Mechanical properties of UHMWPE filled during polymerisation compared with unfilled UHMWPE and Teflon

Property	UHMWPE filled with 30–50 wt%		Unfilled UHMWPE	Teflon
	Calcium carbonate	Kaolin		
Yield point (MPa)	17–19	18–20	20	10
Relative elongation at break (%)	420–500	150–300	500	350–400
Young's modulus (MPa)	1100–1600	1700–3200	770	450–600
Izod impact strength (kJ/m)	NB	20	NB	NB
Linear expansion coefficient ($\times 10$)	0.78	0.78	2.0	0.8–2.5

NB: not breakable

Filled UHMWPE is used where high abrasion resistance is required such as for components of rotor excavators and conveyor belts for handling bulk products. The viscosity of the filled system (filler content > 20 wt%) is too high for methods like injection moulding or extrusion to be used in forming plastic items. Pressing, stamping, and other techniques have been developed for filled UHMWPE. Filled HDPE grades have failed to gain popularity: due to low heat stability and strength they cannot be regarded as engineering materials. They are used only for drainage, sewage, and construction pipes, and mainly in cold climates.

The improvement/reduction in the tensile strength of filled grades is marginal due to stress concentration effects. The modulus is significantly improved on addition of fillers and reinforcements, particularly for glass-fibre-reinforced grades with a suitable coupling agent. The choice of compounding method is very important to limit the effect of fibre length distribution on the mechanical properties of glass-fibre-reinforced PE. Since long glass fibres are damaged under high shear compounding conditions and during injection moulding, knowledge of screw design and moulding conditions is essential for controlling the fibre attrition and reproducibility of product performance. The weld lines in glass-fibre-reinforced components are particularly weak in comparison to other moulded articles, since the reinforcing fibres are oriented perpendicularly to the direction of flow. Therefore, proper care is required in designing mould gates.

3.5.4 Biaxial Orientation

Uniaxial orientation of monofilament and tape is exploited to increase the deformation resistance while uniaxial and biaxial stretching is applied for films. The difference between the original length (or width) of a monofilament, tape, or film and its length after stretching is known as the stretch ratio. After stretching, the material has considerably higher tensile strength (several times than that of unstretched material) and lower elongation at break in the stretch direction. By using suitable rates and temperatures below the crystalline melting temperature, an optimum stretch ratio and hence very high degree of orientation can be obtained.

3.6 Electrical Properties

PE is an excellent electrical insulator (see **Tables 3.1** and **3.9**). PE grades exhibit outstandingly high resistivity, low dielectric constant, and negligible power factor, all substantially unaffected by temperature, frequency (exception is the dissipation factor), and humidity (unaffected by prolonged immersion in water) over the usual range of service conditions. Further, low values of dielectric constant can also be achieved using foamed PE. The power factor is critically dependent on the amount of catalyst residues in the polymer. Typical electrical applications of PE are as insulating material for cable and wires. During ageing, because of incorporation of oxygen-containing groups in the PE structure, the electrical properties are drastically changed, as can be seen from the variation of the dielectric loss factor with oxygen content (**Figure 3.24**).

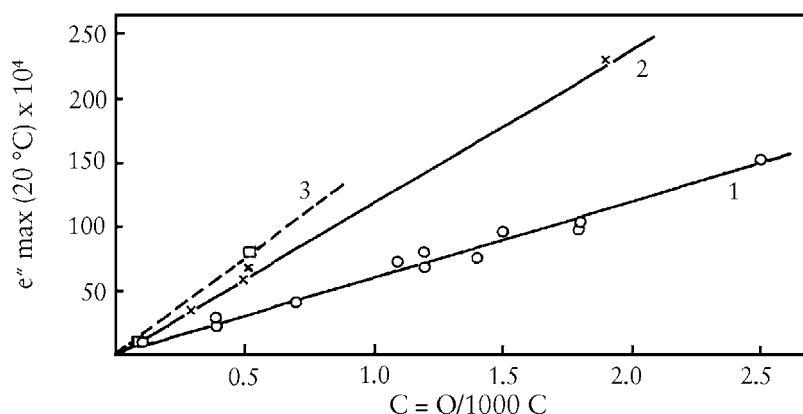


Figure 3.24 Dielectric loss factor at the α maximum at room temperature as a function of oxygen content for oxidised PE of different densities. 1: LDPE, about 20 CH₃/1000 C, $\rho = 0.925$ g/cm³; 2: HDPE, about 4 CH₃/1000 C, $\rho = 0.957$ g/cm³; 3: annealed HDPE, 2 CH₃/1000 C, $\rho = 0.974$ g/cm³ [23]

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3.7 Optical Properties

The optical properties of interest are: refractive index and molecular refraction, polarisation, double refraction (birefringence) of isotropic and oriented PE, clarity, transparency, haze, and gloss (see Tables 3.1 and 3.9). PE granules are white and translucent, but the final appearance varies from hard, rigid, brightly coloured, glossy, flexible or transparent film to high-tenacity fibre. In the melt state the refractive index is 1.4297 and 1.4432 and the molar refraction is 0.3297 and 0.32986 for HDPE and LDPE, respectively.

3.7.1 Transparency

Transparency may be defined as the state permitting perception of objects through or beyond the specimen. It is often assessed as that fraction of the normally incident light transmitted with a deviation of less than 0.1° from the primary beam direction. A material with good transparency will have high transmittance and low haze. Thin films can be transparent or opaque depending on the grade and the processing conditions. The transparency can be improved by control of crystallinity and bi-orientation. The single-phase random copolymers that suppress the formation of crystal structure due to their irregular structure usually have better clarity than homopolymers. It is also important that the refractive index is constant throughout the sample in the line of direction between the object in view and the eye. The presence of interfaces with different refractive indices will cause scattering of light.

Using moulds or dies that provide a very good surface finish improves transparency. Further improvements can be made by choosing processing conditions that restrict the formation of spherulites, e.g., rapid cooling and low melt and mould temperatures. Low mould temperature will reduce the surface gloss of a moulding. Nucleating agents and clarifying agents, which suppress spherulite formation, can improve the transparency. Transparency is improved by contact with liquids to the point where the liquid level inside a container can be seen from outside (contact transparency). Optical transmittance decreases with increasing thickness from 0.9 for a thickness of 0.1 mm to 0.78 for a thickness of 1.0 mm. Birefringence increases with increasing draw ratio.

3.7.2 Gloss

Gloss is defined as the relative luminous reflectance factor of a specimen at the specular angle. Gloss is a function of the reflectance and the surface finish of a material, which, in turn, depends on the finish of the mould.

The workhorse resin used by many extruders is an octene comonomer linear low-density resin with a nominal density of 0.920 g/cm^3 and a melt index of 0.1 g/min . This resin offers a combination of reasonable clarity and toughness. It is also easy to process on most extrusion and converting equipment.

In the past few years the packaging industry has experienced a surge in new designs. These range from zippered, stand-up pouches to high-gloss form, fill, and seal packages for food items. Such packages require low-haze, high-gloss film for sophisticated multicolour graphic printing. The haze and gloss of standard LLDPE does not meet these requirements. Film extruders and converters who are comfortable processing standard LLDPE must make modifications to process narrow MWD metallocene-catalysed PE or use a totally different polymer in their films. A new option is now available to PE film extruders. This LLDPE has improved optical properties over standard LLDPE and has good dart impact and tear strength. The PE will extrude on conventional equipment with no modifications to temperature profiles, die gaps, or screw designs. This PE can be used as a skin, core layer, or both in co-extruded structures. It is also useful for monolayer films. A $24.5 \mu\text{m}$ monolayer film made from this resin has <5.0 haze and >75 gloss properties [39].

3.7.3 Haze: Cloudy or Milky Appearance

Haze is often the result of surface imperfections. Recent developments in sheet manufacturing machinery with two cooling lines, which polish both sides, have resulted in low-haze and high-gloss sheets.

3.8 Surface Properties

The free surface energy for PE is 10 J (at $20 \text{ }^\circ\text{C}$). The critical surface tension for LDPE ranges between 25.5 and 36 mN/m , while for HDPE it varies between 28 and 34.1 mN/m .

3.8.1 Adhesion, Frictional Behaviour, and Blocking

PE, being inert and non-polar, shows low adhesion, i.e., little tendency to bond to a smooth surface. Treatments such as ‘flaming’ or high-energy irradiation introduce polar groups (carbonyl) into the PE surface and improve bonding properties. The coefficient of friction is situated at the lower limit close to that of PTFE. Blocking, defined as that adhesion between layers of film or sheet that prevents their being separated, is a characteristic noted in PE. Slip and anti-blocking agents can be used.

Impact properties are greatly influenced by the testing variables such as stress distribution, testing speed, and temperature, so that different tests may give quite different results.

3.8.2 Modification of Surface Properties

In many applications polyolefins are integrated in different components and composite materials, or they are subjected to more or less ‘aggressive’ media. Two opposite surface characteristics are usually required:

- high surface energy, strong wettability, and polar surface are used for adhesion with other macromolecules, metals, adhesives, paints, and varnishes; and
- low surface energy, weak wettability, and on a non-polar surface are usually required for some biological and industrial applications.

Several practical and economical methods have been developed over the years in order to modify PE surfaces for improved adhesion, wettability, printability, dye uptake, and so on. These methods include mechanical and wet chemical treatments, and gas-phase processes like corona discharge, flame, UV/ozone, glow discharge plasmas, and particle beam bombardment.

UV irradiation of polyolefins may induce changes in their colour and degradation of their physical properties (surface as well as bulk properties). Ozone-generating UV radiation is widely used to clean organic contaminants from various surfaces, while the combined effects of UV radiation and ozone lead to fully oxidised surfaces, increasing the wettability, adhesive properties, and dyeability of polyolefin surfaces.

Surface modification of polyolefins by photografting reactions with acrylic monomers is used as a pre-treatment to improve the adhesion of coatings on polyolefin-based materials by enhancing their hydrophilicity. Fallani and co-workers [40] investigated the behaviour of LDPE pellets (density 0.925 g/cm³; Vicat softening point 98 °C) and mixtures with poly-1,4-butadiene (PB) with a 10.7% molar content of (1,2) units. PI2, an isomeric mixture of alkyl-substituted benzophenones, was used as a photoinitiator. Diethoxybisphenol A dimethacrylate (DEBADM), triallylisocyanurate (TAIC), and 1,6-hexanediol dimethacrylate (HDDMA) were used as crosslinking agents. Irradiation was carried out in air at room temperature using a high-pressure mercury lamp (125 W). **Table 3.12** summarises the results of the modification of two properties of irradiated films. Even if PB softens the films, its presence results in better adhesion of the irradiated layer to the LDPE substrate. All samples show enhanced hydrophilicity.

The impact of *energetic ions* on polymeric materials is very important for the modification of the first few nanometres of the polymer surface. This treatment has disturbing and damaging effects on surfaces, but is also sometimes used to probe surface properties. Bombardment with *low-energy ions* alters the structure, morphology, and chemical properties of materials. The main properties that can be modified using this procedure are rheological properties, electrical conductivity, optical and mechanical properties, surface texture, crystalline state, biocompatibility, and adhesive and surface properties.

On exposing polyolefins to *ionising radiation (fast electrons, γ -rays, and X-rays)*, new chromophore groups can be generated, which efficiently absorb light in the UV, visible, and IR regions. The main effects of electron beam irradiation are chain scission, oxidation and unsaturation (depending on dose rate), and change of oxygen content. The molecular weight can also be modified by this method, due to crosslinking and degradation. Crosslinking increases the modulus and the hardness of a polymer and, in the case of partially crystalline polymers, imparts to the material a non-melting behaviour.

Table 3.12 Properties of surface-treated samples

Sample	Photoinitiator	Crosslinking agent	Young's modulus (MPa)	Water contact angle (degree)
LDPE	–	–	305	125
LDPE/PB (95/5)	–	–	275	116
LDPE	PI2 (3 wt%)	TAIC (2 wt%)	339	85
LDPE/PB (95/5)	PI2 (3 wt%)	TAIC (2 wt%)	376	87
LDPE/PB (95/5)	PI2 (3 wt%)	DEBADM (2 wt%)	328	82
LDPE/PB (95/5)	PI2 (3 wt%)	HDDMA (2 wt%)	350	81

DEBADM: diethoxybisphenol A dimethacrylate
HDDMA: 1,6-hexanediol dimethacrylate
PB: poly-1,4-butadiene
PI2: isomeric mixture of alkyl-substituted benzophenones
TAIC: triallylisocyanurate

Table 3.13 gives the doses of electron irradiation required for crystallographic effects in various polymers. The dose required for the destruction of crystallinity in linear PE is much larger than that for the other polymers, due to the fact that that radiation damage occurs preferentially within the amorphous regions of the material.

On exposure of polyolefins to different *gas plasmas*, functionalisation and crosslinking are observed. All polyolefin surfaces incorporate oxygen after exposure to air, whatever the gas phase. PE and PP differ both from the point of view of incorporated oxygen and stability. The extensive crosslinking of PE and the large amount of oxygen-containing surface groups explain its stability.

The long-term stability of a modified polymer surface is an important factor for the further utilisation of the material. This stability depends on the storage environment as well as on the treatment conditions. ‘Saturation’ (the level for which no more oxygen is incorporated by further treatment) and ‘stable’ (the modification level below which no measurable amounts of material are removed by rinsing with a polymer non-solvent, e.g., methanol) treatment levels were determined for argon-plasma-treated PE and PP [41]. Stable surfaces are characterised by a high selectivity towards C–O functionalities and low levels of ketonic/carboxylate and carbonate functionalities. Saturated surfaces exhibit more carboxylate and carbonate functionalities, present as low molecular weight material, which is subsequently removed upon rinsing (Table 3.14). In terms of oxygen incorporation, the ‘saturation’ and ‘stable’ treatment levels are higher for LDPE than for PP. Also, the depth of modification is greater in LDPE than in PP. This behaviour is explained by the differences between the probabilities of crosslinking and of chain scission for the two polymers.

Table 3.13 Doses of electron beam irradiation required for crystallographic effects in various polymers [23]

Polymer	Dose (C/m ²) necessary for the destruction of crystallinity
Linear PE	102 ± 4
Polyvinylidene fluoride, α-phase	31 ± 2
Polyvinylidene fluoride, β-phase	39 ± 2
Polyvinylidene fluoride, γ-phase	36 ± 2
Polytetrafluoroethylene	14 ± 1

The measurement uncertainties reflect the standard deviation for 7–10 measurements. PE crystals were grown from a dilute solution in p-xylene

Table 3.14 O/C ratio and C1s peak fitting results for argon-plasma-treated LDPE and PP [23]

Sample	O/C ratio	Percentage of carbon in different functionalities (from C1s peak fitting)			
		C–C, C–H	C–O	C=O	CO ₃
LDPE		100	0	0	0
Stable		86.5 ± 1.1	7.9 ± 0.8	3.1 ± 0.4	0.6 ± 0.3
Saturated	0.72 ± 0.03	80.3 ± 1.1	8.2 ± 0.8	5.1 ± 0.4	1.8 ± 0.3
Rinsed	0.16	82.8 ± 1.6	8.4 ± 1.1	4.3 ± 0.4	0.0 ± 0.3
PP		100	0	0	0
Stable		84.3 ± 1.2	9.6 ± 0.6	3.9 ± 0.3	0.5 ± 0.3
Saturated	0.19 ± 0.01	80.6 ± 1.2	8.9 ± 0.6	4.8 ± 0.3	2.1 ± 0.3
Rinsed	0.11 ± 0.01	88.5 ± 0.7	7.0 ± 0.5	2.8 ± 0.3	0.2 ± 0.1

Plasma treatment of PE and PP disposable Petri or assay dishes greatly enhances wetting. Contact angles as low as 22° have been demonstrated for these materials after only a few minutes of oxygen plasma exposure.

Many intravascular devices, such as balloon catheters, are assembled using adhesive bonding of PE components. Chemical surface activation or mechanical surface roughening techniques provide only modest bonding performance, with bond failures noted after as few as eight repeat inflations. With plasma treatment, up to 40 repetitions are achievable. Typical bond strength data are given in Table 3.15.

Material	Without plasma treatment	With plasma treatment
PP	2.55	9.51
LDPE	2.55	10.00
HDPE	2.17	21.50

To increase biocompatibility *in vivo*, the issue of thrombogenesis must be addressed. Many unmodified materials encourage protein binding and thus initiate the process of clot formation. To combat this process, antithrombin coatings are often applied to surfaces. However, when dealing with polymers these antithrombin coatings often fail to bond effectively to the target surface. Using an active gas plasma, surfaces may be modified by heparinising or by grafting of antithrombotic functional groups, which achieve effective chemical bonding to previously inert material surfaces.

In specific cases where cell attachment is necessary to ensure proliferation, plasma-modified *in vitro* cell containers show dramatic improvement over untreated containers. By using surface modification procedures, the performance of PE can be substantially improved compared to the untreated state.

Corona discharge treatments of polyolefins in air proceed through surface oxidation, which is accompanied by considerable chain scission for both PE and PP.

Silent discharge treatments of PE and PP give a similar O/C ratio to that obtained with low-pressure plasma treatments in air.

3.9 Hardness and Scratch Resistance

LDPE is easily marked by a thumbnail, HDPE is scratched in this way with difficulty, but PP is marked little, if at all. Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation, or scratching. Hardness is a relative term and should not be confused with wear and abrasion resistance. Many tests have been devised to measure hardness. Rockwell and Durometer hardness test are commonly used.

3.10 Abrasion Resistance

The resistance to abrasion is closely related to other factors such as hardness, resiliency, and the type and amount of added fillers and additives. The resistance to abrasion depends on factors such as test conditions, type of abrading material, and development and dissipation of heat during the test cycle. It is most often measured by the weight loss when a material is abraded with an abrader after a number of revolutions (at least 5000). The Taber abrader is widely used. For softer materials, less abrasive wheels with a smaller load on the wheels may be used. Wear may be high when reinforced parts are in contact with unreinforced parts. Use of lubricated reinforced grades may reduce wear when in contact with an unreinforced component. The abrasion resistance of LDPE

is 10–15 mg/100 cycles, higher than that of HDPE at 2–5 mg/100 cycles. China clay additives can be used to improve scratch resistance.

3.11 Friction

Friction characteristics are very important for fibre-to-fibre interactions in spin technology. Internal lubricants can be used to reduce the friction, which can be quite important in slide applications such as medical syringes.

3.12 Acoustic Properties

Articles made from HDPE, polystyrene, or ABS have their own resonance and tend to rattle. Some acoustic properties of PE and other plastic materials are given in Table 3.16.

In comparison with PP, which has excellent acoustic damping properties at normal service temperatures, articles made from HDPE, polystyrene, and so forth, have their own resonance and tend to rattle [42].

Plastic material	Velocity, longitudinal (m/min)	Density (g/cm ³)	Acoustic impedance	Attenuation (dB/cm, 5 MHz)
ABS, beige	2230	1.03	2.31	11.1
Acrylic, clear	2750	1.19	3.26	6.4
Bakelite	1590	1.40	3.63	–
Cellulose butyrate	2140	1.19	2.56	21.9
EVA, 18% acetate	1800	0.94	1.69	–
EVA, 28% acetate	1680	0.95	1.60	–
Polycarbonate, Lexan	2300	1.20	2.75	23.2
Kodar PETG copolyester	2340	1.27	2.97	20.0
Nylon 6.6	2600	1.12	2.90	2.9
Nylon 6.6, black	2770	1.14	3.15	16.0
Polycarbonate, clear	2270	1.18	2.69	24.9
PE	1950	0.90	1.73	–
HDPE	2430	0.96	2.33	–
LDPE	1950	0.92	1.79	2.4
Polyethylene oxide	2250	1.21	2.72	–
PP, white	2660	0.89	2.36	18.2
Polystyrene, Styron 666	2400	1.05	2.52	1.8
Polyvinyl butyral	2350	1.11	2.60	–
Polysulfone	2240	1.24	2.78	4.25
Styrene butadiene	1920	1.02	1.95	24.3
Dimethyl pentene polymer	2200	0.83	1.84	3.8–4.4
<i>PETG: polyethylene terephthalate glycol</i>				

3.13 Degradation Behaviour

The durability of organic materials exposed to the outdoor environment is determined to a large extent by incident solar radiation. While other weather factors contribute to limiting the lifetime of a material exposed to outdoor conditions, the absorbed solar energy is mainly responsible for the

destructive effect of the weather, having the greatest potential for breaking chemical bonds. Heat, moisture, oxygen, and other factors generally promote ageing through their influence on secondary reactions, following the primary bond breaking reactions by light. For outdoor applications of polymers, additives like UV absorbers and light stabilisers are generally used during compounding, which are transparent to solar radiation but immune to the destructive effect of UV radiation.

It is well known that the degradation of PE exposed to heat and/or UV radiation involves thermo- and/or photo-oxidation. Thermal degradation temperatures range between 335 and 450 °C. Polyolefins do not absorb at wavelengths greater than 290 nm, being transparent to terrestrial sunlight. However, they photodegrade in outdoor use because of the initiation by impurity chromophores that they contain, such as peroxides and hydroperoxides, carbonyl groups, unsaturation, and metal salts. The concentration of impurities increases upon thermal processing, having a detrimental effect on light stability. Both carbonyl and hydroxyl content are found to increase steadily with UV exposure, together with the amount of volatile products, mainly water, CO, CO₂, CH₄, acetone, and methanol. These chemical changes are associated with a severe reduction in the elongation at break and a loss of the tensile strength. The deterioration of the properties depends on absorbed dose, oxygen permeability, crystallinity of polymers, and so on. Some photoactive oxides such as ZnO or TiO₂ exhibit a catalytic activity in the photo-oxidation of polyolefins.

Particulate, inorganic additives (fillers) are commonly added to commercial thermoplastic and thermosetting resins to achieve economy, as well as to modify favourably certain properties, such as stiffness, heat distortion, and moulding. Photosensitisers are used to prevent waste accumulation.

Based on the findings of accelerated weathering by xenon tests and natural (outdoor) weathering for films of LLDPE and LDPE resins, it was concluded that PE films containing additives, particularly hindered amine stabilisers (HAS), have a UV stability four times higher than the corresponding pure films [43].

3.13.1 Photo-oxidation

Commercial extrusion-grade HDPE (with a density of 0.9537 g/cm³ and a melt flow index of 0.32 g/10 min) unfilled or containing a mineral filler [calcium carbonate (CaCO₃) with an average particle size of 0.1 mm and a density of 2.70 g/cm³] was exposed to UV radiation [44]. Over the entire exposure time, the HDPE crystallinity grew linearly, whereas its melting temperature decreased (Figure 3.25). This increase of crystallinity can be attributed to the preferential polymeric chain oxidation that affects the amorphous phase of HDPE, as well as to the formation of new crystallites

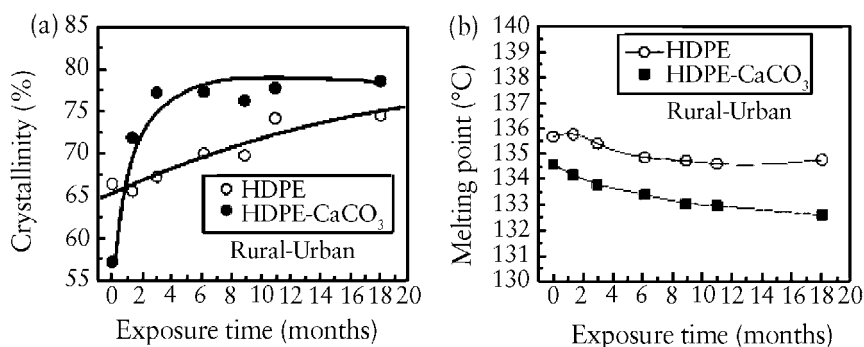


Figure 3.25 Variation of (a) crystallinity and (b) melting temperature for HDPE and HDPE–CaCO₃ samples exposed to natural weathering conditions [44]

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induced by chain scission reactions. An intrinsic characteristic of these small new crystalline regions should be a lower fusion temperature. The HDPE–CaCO₃ crystallinity grows exponentially during the first six months after which it stabilises at around 77–80%, while its melting point decreases with exposure time. All the results obtained lead to the conclusion that the mineral filler induces chain scission reactions during the degradation and accelerates this process.

In another experiment, samples of LDPE were aged at an accelerated rate with QUV weathering tester equipment, using a UVB fluorescent bulb of 0.60 W/m² irradiance (at 313 nm), with eight hour cycles of UV irradiation at 60 °C and an additional four hours of deionised water spraying at 50 °C, with the incident beam at 90°. The samples were submitted to ageing for 12, 24, 50, 100, 200, 400, and 800 hours [45]. It was observed that the hardness and elastic modulus values increased from surface to bulk with ageing time. The modifications in the elastic modulus with ageing were high enough to promote cracking at the surface for exposure times of 400 hours and above, and were attributed to a continuous variation of the modulus with depth.

3.13.2 Thermal Degradation

The sensitivity of polymers to temperature variations is determined by several factors such as the residual content of impurities (peroxide or catalyst) remaining after manufacture.

The thermal degradation of different types of EVA was carried out at three temperatures (150, 175, and 200 °C) in an isothermal oven [46]. A change in crystallinity is the first process that takes place in the early stage of heating. This is followed by other phenomena, the most important of which is the oxidation of the polymer matrix starting from 235 °C (Table 3.17).

Pipes of HDPE were exposed to chlorinated water at elevated temperatures. The materials were stabilised with hindered phenols and phosphites [47]. Measurement of the oxidation induction time showed that the stabilising system was rapidly chemically consumed by the action of chlorinated water. Extensive polymer degradation of the unprotected inner wall material occurred, confined strictly to the surface and to the amorphous phase of the semi-crystalline polymer. It was obvious that the species responsible for the loss of the antioxidant must be soluble in the polymer, but not very reactive with the polymer itself.

Blown films of LDPE containing a totally degradable plastic additive were submitted to a thermo-oxidative degradation treatment in air in an oven at 55 °C for 44 days [48]. A significant increase of the original weight of the test sample was recorded after 11 days, most likely due to oxygen uptake by the polymer matrix induced by the pro-oxidant additives. For the mechanical properties, an initial increase of the strength was recorded, followed by a fast decrease of the film integrity after

Table 3.17 Main processes occurring in EVA materials during heating

Temperature (°C)	EVA (27–29% VA content)	EVA (32–34% VA content)	Process
70	Endothermic	–	Crystallinity modification
175	Exothermic	–	Volatiles removal
235	Endothermic	–	Initial oxidation
270	–	Exothermic	
290	Endothermic	–	
305	Endothermic	–	Chain oxidation forming intermediates
310–325			
325–335	Exothermic	Exothermic	
355	Endothermic	Endothermic	Oxidation ends

11 days as a result of the fragmentation of the polymer chains. The initial increase of the strength at break was accompanied by an analogous behaviour in the strain property. This behaviour could be attributed to a sort of plasticisation effect exerted by a low molecular weight fraction produced in the first stage of the thermo-oxidative degradation of the polymer matrix, as suggested by the initial increase of the specimen weight during the same timescale. Crosslinking may also occur through unstable peroxide bridges.

Gorghiu and co-workers [49] assessed the thermal stability of various sorts of PE used as insulating materials in electrical cable manufacture. The essential problem of the long-term operation of wires and cables is the durability, the measure of the chemical resistance of the material. They developed a chemiluminescence study of the thermal degradation of several PE (LDPE, LLDPE, HDPE, UHMWPE) in the presence of triazines as stabilisers. The kinetic effects of metals (aluminium, copper, iron, manganese molybdenum, titanium and zinc) were assessed at 200 °C by the calculation of the oxidation induction period, half-oxidation time, maximum oxidation time, and rate in the propagation stage. It was established that the presence of two triazines for the prevention of oxidation of macromolecular substrates allowed the ordering of the PE by their oxidation resistance. For triazine T5: UHMWPE >> HDPE > LDPE > LLDPE; for triazine T7: UHMWPE >> HDPE > LLDPE > LDPE.

3.13.3 Degradation by High-energy Radiation

Low dose (0–60 kGy) irradiation is used both for the improvement of long-term properties (crosslinking of PE pipes, cables, and so on) and for medical applications. For the sterilisation of medical items, a dose of 25 kGy of ⁶⁰Co γ -rays can be used to destroy bacteria, fungi, and spores.

At higher doses, in the presence of oxygen or over a long period of time, degradation occurs. Radiochemical degradation occurs by three distinct, simultaneously competing processes: oxidative scission in amorphous phases, crosslinking, and crystal destruction and/or chemocrystallisation. Chemocrystallisation induces only an apparent increase of crystallinity and of density, observed in PE oxidation, due to the formation of polar groups (–OH, –C=O, –COOH) that increase the intermolecular forces of attraction resulting in a high density [50, 51]. The dominance of one of these mechanisms over the others is strongly dependent on the irradiation conditions. Radiation-induced oxidative degradation is dependant on the total dose rather than on dose rate, if the polymer matrix contains stabilisers like antioxidants. Mechanical properties are found to worsen with increasing irradiation dose. Higher contents of antioxidants used in polymers reduce the extent of polymer crosslinking. These antioxidants also influence polymer network formation during compounding as well as the radical yield during irradiation.

Crosslinking of UHMWPE leads to a reduction of the degree of crystallinity. Tensile tests performed on UHMWPE and crosslinked UHMWPE show that there is a monotonic reduction in the yield stress, ultimate tensile stress, and strain-to-break with an increase in the degree of crosslinking. One of the causes for the degradation of UHMWPE in artificial joints may be linked to the sterilisation treatment employed before surgery. The oxygen uptake in UHMWPE increases upon irradiation and continues to do so as the material ages. The scission process is especially important to the structural integrity of the polymer over time, as long chains are thus able to pack together more easily, leading to a lower molecular weight material with higher crystallinity and density (similar to HDPE after self-ageing for five years). This evolution is further complicated by oxidative degradation, which can stiffen the molecular chains and lead to embrittlement and a reduced fatigue and wear resistance. This structural evolution may be responsible for the limited life of this type of polymer component, currently 15 years or less.

LLDPE treated with γ -rays is characterised by an improvement of the thermal stability. Young's modulus is found to increase with increasing radiation dose, although radiation crosslinking does not significantly influence the yield strength. Elongation at yield, elongation at break, and strength at break are found to depend strongly on radiation dose [52].

Exposure to γ -rays of some EVA-type elastomers was performed at room temperature in a Gamacell irradiation device provided with a ^{137}Cs source (dose rate 0.5 kGy/h). The selected doses were 50, 100, 150, 200, and 250 kGy [46]. High-energy radiation exposure of EVA caused a severe depletion of acetate units. A significant decrease in the acetate content occurred for the first 150–200 kGy of radiation, this energy being sufficient to break strong bonds like C–O or C=O. Irradiation and heating of EVA in the presence of oxygen affect the molecular structures by means of the scission of acetate units and of various reactions of α -hydroperoxides. In both routes, carbonyl units and unsaturation accumulate with increasing transferred energy. An opposite effect is found for PE, which offers higher stability to the destructive action of thermal or radiation energy.

UHMWPE was treated with γ -rays using ^{60}Co industrial radiation equipment with an operating dose rate of 2.5 kGy/h at room temperature in air. The test specimens were exposed directly to integrated doses of 100, 250, 350, 500, 1000, 1500, or 2000 kGy [53]. The tensile properties of the irradiated material are summarised in Table 3.18. The longitudinal and transverse results are quite close, suggesting that the material is almost isotropic. The tensile properties change with irradiation. The non-irradiated samples and the samples irradiated with 100 kGy have high strength and plasticity. As the dose increases the material undergoes a gradual change from ductile to brittle behaviour, with a significant decrease in the elongation at break. The tensile ductile-to-brittle transition of UHMWPE suggests that irradiation produces chain scission. Scanning electron microscopy and electron spin resonance data confirm that oxidation of free radicals takes place in stages, principally in the near-surface regions. The molecular structure of UHMWPE on treatment with γ -rays is modified, the degradation being attributed to chain scission followed by an oxidative process.

Dose (kGy)	Maximum strength (MPa)		Elongation at break (%)	
	Longitudinal	Transverse	Longitudinal	Transverse
100	33.1	27.0	410	318
250	22.2	24.4	31.1	24.4
500	23.5	23.3	31.3	23.3
750	24.5	24.1	30.6	24.1
1000	24.1	24.8	33.0	24.8
1250	25.3	27.0	26.9	27.0
1500	25.7	26.3	28.2	26.3
1750	25.5	26.4	28.4	26.4
2000	26.4	27.4	28.4	27.4

3.13.4 Biodegradation

It is frequently asserted that polyolefins cannot biodegrade since the molecular weight must be less than 500 for this to occur. The resistance of PE to biological attack is related to its hydrophobicity, water repellency, high molecular weight, and lack of functional groups recognisable by microbial enzymic systems. All of these properties limit applications in which biodegradation is a desirable attribute. However, it has been demonstrated that, while normal commercial PE do not biodegrade, those formulated with transition metal pro-oxidants (notably iron complexes), after ageing or weathering by exposure to UV radiation, support microbial growth. Pro-degradants include additives such as polyunsaturated compounds, transition metal ions, and metal complexes (e.g., dithiocarbamates), which render PE, and polyolefins in general, susceptible to hydroperoxidation. The functional groups provided act as initiators of thermo- and photo-oxidation of hydrocarbon polymer chains. These abiotic degradation processes result in functional macromolecules, which thermally and/or photochemically cleave repeatedly to give low molecular weight fragments,

especially in the presence of transition metal ions. These low molecular weight oxygenated products include aliphatic carboxylic acids, alcohols, aldehydes, and ketones.

In order to overcome pollution problems, the possibility of a combined photo- and bio-degradation process has been investigated, in which degradation started by the former can be completed by the latter, ultimately converting a plastic to useful humus, water, and carbon dioxide. Pre-ageing by either light or heat has been shown to be an essential abiotic precursor to biodegradation. Low molar mass oxidation products can then be rapidly bioassimilated by thermophilic micro-organisms. Albertsson and co-workers have shown that a wide range of biodegradable oxidation products are formed in the abiotic peroxidation process [54].

It was shown in a study of a commercial photo-biodegradable PE (Plastor1) that low molar mass products are removed from the surface of the polymer by bioerosion without significantly affecting the molar mass of the bulk polymer. The biodegradation of photodegradable PE begins at $M_w = 40,000$ and it was concluded that photoinitiated peroxidation is the rate-determining step in the biodegradation of polyolefins in sunlight [55].

Degradable PE samples were sterilised by UV exposure at 254 nm (2×5 min) and inoculated over 30 minutes with a suspension of different strains (bacterium and fungus). Assays and controls were incubated for six months at 27 °C and 85% humidity in an environmental cabinet. Cultivations were carried out in Petri dishes containing glass beads and a mineral salt medium [56]. It was observed that the heated films oxidised more rapidly than the control at the end of the induction period.

Ageing of compacted films (obtained by compression moulding at 100 °C) led to a reduction in the molecular weight. Samples stored at 20 °C showed a quite important reduction in M_n and M_w , with a narrowing of the MWD, whereas samples pre-oxidised at higher temperatures showed molecular enlargement. However, after incubation with micro-organisms, the higher molecular weight material disappeared and the distribution became similar to that of the samples oxidised at lower temperatures. It can be concluded that under conditions where oxygen diffusion is a limiting factor, for example, in thick sections of polymer, $-C-O-O-C-$ (and possibly but less likely $-C-O-C-$ and $-C-C-$) bonds may be formed in the polymer at higher temperatures. The peroxide crosslinks dissociate slowly in the biotic environment. Molar mass reduction due to the action of micro-organisms does not occur to any significant extent during incubation, the main role of the micro-organisms in this process being to scavenge the low molecular weight oxidation products as they are formed. That is, the abiotic peroxidation process is the rate-determining step.

Non-degraded and thermally fragmented ($M_w = 6.72$ kDa) LDPE film samples containing totally degradable plastic additive (TDPA) pro-oxidants [47] were subjected to respirometric biodegradation tests. It was observed that LDPE-TDPA oxidised samples underwent significant biodegradation (50–60% by carbon dioxide evolution) over a period of 18 months as mediated by soil micro-organisms in closed respirometric vessels.

3.14 Biological Behaviour

3.14.1 Assessment Under Food and Water Legislation

The main requirements for contact with food are that the article must not impart odour or taste to the food and should be suitable for the intended application. Additives, monomers, catalyst residues, polymer degradation products and so on can migrate into any food in contact if the concentration of these substances is lower in the food than in the plastic. The migration is dependent on temperature and time; the rate of migration is inversely proportional to molecular weight. The migration of these species could produce toxicity or the formation of undesirable flavours or odours, known as organoleptic problems.

Application of PE in contact with food and water is covered by the relevant standards/regulations of different authorities in different countries. Health assessment of plastics under food legislation varies from one country to another. Normally the migration/extraction of resins and additives is measured for contact with different food simulants. For example, distilled water, vegetable oil, or acetic acid. The degradation of materials during processing, the use of mould-release agents and so on can make the final products noncompliant.

3.14.2 Resistance to Micro-organisms

PE is not a nutrient medium for micro-organisms and is therefore not attacked by them. It cannot be penetrated by micro-organisms provided the wall or film thickness is at least 0.1 μm . In thinner walls, small pores may be introduced during manufacture. Low molecular weight additives such as plasticisers, lubricants, stabilisers, and antioxidants may migrate to the surface of plastics and encourage the growth of micro-organisms. The detrimental effects can be readily seen through the loss of properties, change in aesthetic quality, loss of optical transparency, and increase of brittleness. Preservatives, also known as fungicides or biocides, are added to plastic materials to prevent the growth of micro-organisms.

3.14.3 Physiological Compatibility

Biocompatibility tests are designed to determine the risk of adverse health effects from the use/abuse of materials. The toxicity of a material depends on the toxicity of the added ingredients and their migration into the body. Potential toxic substances include plastic additives (antioxidants, stabilisers, plasticisers), processing aids (lubricants, mould release agents, cleaning agents), and products from polymer degradation during storage or implantation. ISO 10993 – *Biological Evaluation of Medical Devices* [57] outlines the methods for evaluating the safety of medical devices, directly or indirectly in contact with the body or with bodily fluids. The extent of testing depends on the duration of contact, the nature of contact with the body (externally or internally), and the body part in contact (skin, mucous membrane, breached or compromised surfaces, blood, tissue, bone, etc). Most of the PE grades approved for food contact applications are normally suitable to produce articles for pharmaceuticals and medicines.

3.15 Biocompatibility

The most appropriate interpretation of biocompatibility for PE biomaterial applications is that the biocompatibility be defined in terms of the success of a device in fulfilling its intended function. For example, for a hip joint prosthesis, one must take into consideration the fatigue resistance of the device, its corrosion resistance, the distribution of the stresses transferred to the bone by the device, the solid angle of mobility provided, and the overall success of the device in restoring a patient to an ambulatory state. The performance of a hip joint prosthesis might also be assessed in terms of the tissue reaction to acetabular cup. The performance of individual materials is sometimes referred to as ‘biocompatibility’ and sometimes as ‘bioreaction’. Hardness, shape, porosity, and specific implant site are very important [58].

Along with PP, PTFE, and polyesters, PE is used for sutures, soft tissue augmentation, vascular prosthesis, implants, and so on.

Oriented PE foils, 10 μm thick with a molecular weight of 1.8×10^5 and a density of 945 kg/m^3 , were irradiated with 10 and 63 keV Ar^+ ions at fluences from 10^{17} to $3 \times 10^{19}/\text{m}^2$. The ion beam current density was below 50 nA/cm^2 and the pressure in the implanter chamber was 10^{-3} – 10^{-4} Pa. The irradiated specimens were exposed to solutions of 2 wt% alanine [$\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$] in water, at room temperature, for 12 hours [59]. The adhesion of 3T3 rat fibroblasts on the modified PE was studied *in vitro*. The radiation damages to the polymer chain, such as free radicals and

excessive double bonds, are the sites on which the alanine is grafted. Alanine grafting increases the surface polarity and decreases the electrical conductivity of the PE. It was found that an increase in surface polarity caused an increase in cell adhesion. However, when its value was too high, cell adhesion started to decrease. In general, higher cell adhesion was observed on modified PE compared to unmodified PE.

3.16 Wear Properties

HDPE is a rugged material, which is easy to mould, has a high resistance to impact, and is not affected by most chemicals. Principally used in injection and blow moulding, it may also be vacuum formed or extruded. The working temperature range is -35 to $+65$ °C.

Wear resistance is of special interest for PE used in orthopaedic implants. For more than 30 years UHMWPE has been used as a bearing material in total joint replacement prostheses. Such orthopaedic implants usually comprise a metal (typically a cobalt–chromium alloy) or ceramic component that articulates against a UHMWPE component during *in vivo* use. It has been well established that the longevity of such implants depends on the wear performance of the UHMWPE components. The presence of particulate wear debris of UHMWPE that is generated due to the sliding of UHMWPE components against metal or ceramic counterfaces has been linked to complications such as tissue inflammation, bone loss (or osteolysis), and implant loosening. Osteolysis resulting from wear of UHMWPE is recognised as the leading problem in orthopaedic surgery today.

Although UHMWPE has superior wear characteristics compared with other polymers, its resistance to wear must be improved to increase the lifetime of joint replacement prostheses. New formulations of UHMWPE have been developed in the past, with the goals of reducing creep and wear rates. For example, UHMWPE has been blended with carbon fibres to fabricate total joint replacement components. The material is known as Poly Two (Zimmer Inc., Warsaw, IN, USA). However, while the devices manufactured using this blend had excellent resistance to creep, there was a decrease in fatigue resistance. In addition, no improvement in wear resistance was observed, and the material was ultimately discontinued for use in joint replacement devices. More recently, high-pressure crystallisation has been used to produce UHMWPE components with improved mechanical properties such as increased yield stress and Young's modulus. However, this material, known as Hylamer (DePuy-DuPont Orthopaedics, Newark, DE, USA), has again not shown any improvement in laboratory wear tests, despite enhanced creep resistance and an increase in resistance to fatigue crack growth. Early clinical results also indicate that Hylamer does not demonstrate increased resistance to wear in total hip replacement prostheses compared with conventional UHMWPE.

In recent years a new approach has been adopted to improve the wear performance of UHMWPE. Instead of using novel processing methods such as high-pressure crystallisation or physical blending, UHMWPE components have been modified via chemical methods. Crosslinking of UHMWPE macromolecules has been performed using crosslinking agents such as peroxides, and through γ -ray or electron beam irradiation. The crosslinking of UHMWPE results in an interpenetrating network of high-molecular-weight PE chains, with the potential benefit of increased strength in the interfacial region between resin particles of PE components. Incomplete consolidation of resin particles has been observed in components of UHMWPE, and is believed to contribute to wear. While there have been previous investigations of the effects of crosslinking on PE morphology and mechanical properties, these are the first studies that demonstrate the advantage of crosslinking UHMWPE for use in total hip replacement prostheses. Laboratory hip-simulator wear tests have shown that there is a decrease in UHMWPE wear rate corresponding to an increase in the degree of crosslinking. However, it should be noted that these studies have not yet addressed the resistance of crosslinked UHMWPE to third-body wear. This is the abrasion that results from the presence of hard particles that do not originate from either the UHMWPE or the metallic articulating component (for example, bone chips, bone-cement particles, or debris from the metallic stem).

Although crosslinking of UHMWPE has been shown to improve performance in hip-simulator wear tests, mechanical tests conducted on crosslinked material have shown deterioration in several mechanical properties including Young's modulus, yield stress, ultimate tensile stress, and strain to break. These results appear contradictory, since it is generally believed that the toughness of a polymer correlates with its wear performance. A better understanding of the relationship between the mechanical properties and wear performance of UHMWPE is required for the development of new wear-resistant polymeric components for use in total joint replacement prostheses.

Wear in conventional UHMWPE has been measured at 30 mm³ per million cycles. Some of the macromolecules combine with each other to produce crosslinks. The amorphous region is susceptible to large-strain plastic deformation while the crystalline region imparts strength and toughness to the material. The arrangement of macromolecules and crystallites that explains wear and mechanical behaviour is shown in **Figure 3.26**.

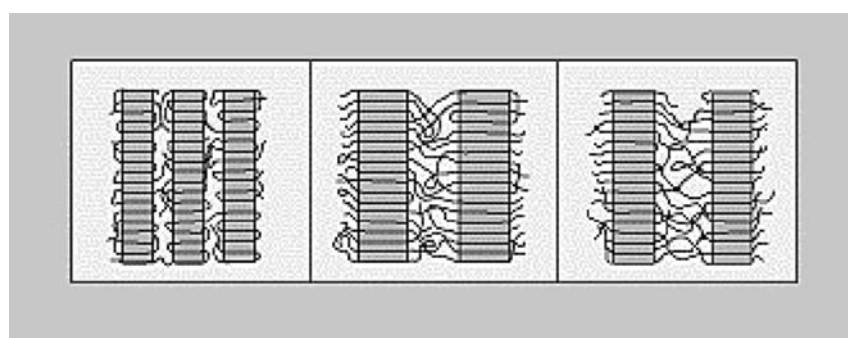


Figure 3.26 Schematic representation of the arrangement of macromolecules of PE and crystallites of HDPE (left), UHMWPE (centre), and crosslinked UHMWPE (right)

The oxygen diffusing from the outside, in time, leads to chain scission recrystallisation and embrittlement of the material, thus decreasing the wear resistance. The melt-irradiated UHMWPE is expected to have long-term resistance to oxidative degradation as a bearing surface in total hip replacement with no measurable wear at 2.6 million cycles. Crosslinking of the PE effectively increases the intermolecular connections in the amorphous region and makes it resistant to large-strain plastic deformation. Entanglements play an important role in wear resistance and must be increased to improve the wear performance of UHMWPE.

Electron beam irradiation can be delivered faster than that of γ -rays and can be carried out while the material is hot. Electron beam irradiation has limited penetration. A voltage of 3 MV delivered by the irradiator used in one study led to a penetration depth of only 1 cm. The procedure consists of irradiation of the material in the molten state, which is then roughly shaped into an acetabular component. This is followed by re-machining the final shape of the acetabular component [50, 51, 60-63].

3.17 Molecular Properties

Various molecular parameters are as follows: characteristic ratio: 6.7; bond angle: 112°, slightly larger than the tetrahedral value of 109° 28'; bond length: 0.153 nm; equivalent chain $L_{\text{equiv.chain}}$: 1.23 nm. Solubility parameters are 16.4 MPa for HDPE and 14.3 MPa for LLDPE. These figures were obtained from: <http://gozips.uakron.edu/%7Emattice/ps674/pe.html>.

3.17.1 IR Spectra

PE is a special case due to the absence of bulky side chains, allowing close interaction of the backbones of neighbouring chains. Hence its IR spectra are considerably different from those of low molecular weight compounds (Figure 3.27). It is worth remarking that the polymer with the simplest chemical structure of its repeating structural unit has one of the most interesting IR spectra. The IR spectra of commercial products have supplementary bands, because of the contribution of impurities, chain defects, and so on. The assignments of the bands are given in Table 3.19 [64].

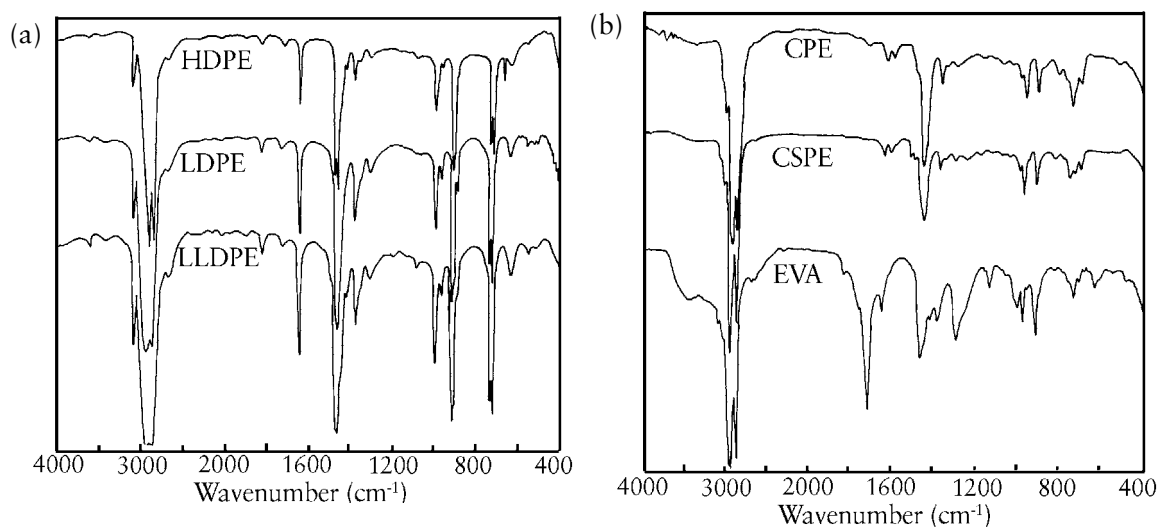


Figure 3.27 IR spectra of basic types of PE and copolymer [65]

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The characteristic bands of the possible branches, such as methyl, ethyl, amyl, hexyl, and long-chain branches, are found in the 1320–1400 cm^{-1} region, which, after deconvolution, can be used for quantitative determination. Unsaturated structures are identified in the 800–1000 cm^{-1} region (ASTM D3124-98 [66]). These include terminal vinyl (910 cm^{-1}), *trans*-vinylidene (965 cm^{-1}), and vinylidene (888 cm^{-1}).

The structural properties for two PE grades are given in Table 3.20.

In the crystalline regions, the chain is a planar zig-zag with all *trans* placements at the C–C bonds. In the common crystal form, with an orthorhombic unit cell, there are two $\text{CH}_2\text{--CH}_2$ groups per unit cell. Crystal field splitting, as at 733/721 and 1460/1475 cm^{-1} , is directly an effect of the crystal, and not just the preferred conformation of a single chain. This offers a solution for the evaluation of the relative crystallinity of materials.

3.17.2 Crystals

Lamellae have a variety of sizes and imperfections including planar zig-zag of crystalline PE chains. The lower molecular weight chains crystallise more rapidly than the higher molecular weight chains. There are kinetic effects. The melting temperature and range will also depend on how carefully the sample is crystallised, i.e., the size of the undercooling. From melt and solution an orthorhombic structure is obtained, cold stretching gives a monoclinic form, and crystallisation under pressure leads to a hexagonal structure. The repeating pattern is *trans* (there is a *trans* state at every bond). The structure has two methylene groups per ‘turn’, or per repeat.

Band position (cm ⁻¹)	Band intensity*	Assignment**		Terminal groups, impurities
		Crystalline	Amorphous	
720	fi	r (CH ₂)	r (CH ₂)	
731	fi	r (CH ₂)		
888	fs			R'RC=CH ₂
890	ffs			r (CH ₂)
908	fs			RCH=CH ₂
964	ffs			<i>trans</i> -RCH=CHR'
990	s			RCH=CH ₂
1050	fs	t (CH ₂)		
1065	fs		v (C-C)	
1078	fs		v (C-C)	
1110	ffs			
1131	ffs		v (C-C)	
1150	fs			
1170	ffs		r (CH ₂)	
1176	fs	w (CH ₂)		
1185	ffs			
1303	m		t (CH ₂)	
1353	m		w (CH ₂)	
1369	m		w (CH ₂)	
1375	m			δ _s (CH ₃)
1436	fs		δ (CH ₂)	
1457	ffs			δ _a (CH ₃)
1463	fi	δ (CH ₂)	δ (CH ₂)	
1473	fi	δ (CH ₂)		
1640	fs			v (C=O)
1722	fs			v (C=O)
1737	ffs			v (C=O)
1894	s	1154+731		
2850	ffi	v (CH ₂)		
2857	ffi	v (CH ₂)		
2874	s			v (CH ₃)
2899	ffi	v (CH)		
2924	ffi	v (CH)	v (CH ₂)	
2960	s			v (CH ₃)

* Band intensity: s: weak; m: medium; fi: intense; ffi: very intense; ffs: very weak
 ** Vibration type: v: stretching; r: rocking; δ: bending; w: wagging; t: twisting
 Subscripts: s: symmetric; a: asymmetric

Molecular property	LDPE	HDPE
Branches	20–30 ethyl and butyl branches/1000 carbons	Mainly linear, <10 ethyl branches/1000 carbons
Number of double bonds/1000 carbons	<0.3	<0.2
Type of unsaturation (ASTM D3124-98 [64])	Vinylidene	80
	Vinyl	10
	<i>Trans</i> -vinylidene	10
		30
		45–100
		20

3.17.3 Radii of Gyration

For a PE chain with $M = 100,000$, the minimum radius of gyration is 3.3 nm, calculated using a partial specific volume of $1.43 \text{ cm}^3/\text{g}$. For a freely jointed chain, the value is 5.3 nm, calculated using a bond length of 0.154 nm and a molecular weight per bond of 14. For a freely rotating chain the value is 7.5 nm, calculated using a bond length of 0.154 nm, a molecular weight per bond of 14, and a tetrahedral bond angle. For a chain with symmetric hindered rotation about independent bonds, the value is 10 nm, calculated using a bond length of 0.154 nm, a molecular weight per bond of 14, a tetrahedral bond angle, three states with torsion angles of 180° , 60° , and -60° , an energy of 2 kJ/mol for the two *gauche* states, and $T = 140^\circ\text{C}$. For a chain with pairwise interdependent bonds, the value is, via the rotational isomeric state model, 14 nm, calculated using a bond length of 0.154 nm, a molecular weight per bond of 14, a tetrahedral bond angle, three states with torsion angles of 180° , 60° , and -60° , an energy of 2 kJ/mol for the two *gauche* states, an energy of 8 kJ/mol for the pentane effect, and $T = 140^\circ\text{C}$. For the approximation of a fully extended chain, the value is 183 nm, using a bond length of 0.154 nm, a molecular weight per bond of 14, and a tetrahedral bond angle. The temperature coefficient is $-0.0011/^\circ\text{C}$.

3.17.4 Unit Cell Parameters

The unit cell parameters are given in Table 3.21.

	LLDPE	LDPE	HDPE	
Crystal system	Triclinic	Orthorhombic stable; monoclinic	Orthorhombic	Monoclinic, metastable
a (Å)	4.285	4.285	7.417	8.09
b (Å)	4.82	4.82	4.945	2.53
c (Å)	2.54	2.54	2.547	4.79

3.17.5 X-ray Scattering

A single crystal of low molecular weight material gives the most detailed X-ray diffraction patterns, from which the structure of the molecule can be reconstructed. Consider instead a powder pattern, obtained from many very small crystals that are randomly oriented in the sample. The discrete spots characteristic of the single crystal now become rings instead. A densitometer is used to scan the intensity of the scattered radiation along a line stretching radially from the transmitted beam. Rather sharp lines are seen with fairly large crystals (Figure 3.28(a)). Smaller crystals give broader lines (Figure 3.28(b)). A melted (amorphous) sample exhibits a very broad line (or halo) and sometimes weaker, secondary lines. Some residual local order persists in the amorphous state.

There is some evidence for the existence of polymorphic forms in PE. Semi-crystalline polymers exhibit amorphous and powder features simultaneously. The amorphous halo is seen when the alkane is raised above its melting temperature. Semi-crystalline PE exhibits the amorphous halo, with sharp lines (but perhaps broader than for the *n*-alkane) superimposed.

3.17.6 Polymer Morphology

Polymer morphology deals with the form and structure of polymers that result from aggregation of crystals. Two different morphological forms may be distinguished: spherulites (assemblages of crystals radiating from a point in all directions) and single crystals. The orientation of the polymer molecules in spherulites is perpendicular to the spherulite radii; that is, tangentially oriented within the spherulite. As to fine structure, spherulites are composed of a radiating fibrous structure, and the fibril appears to be the basic unit of the spherulite, composed of thickly packed lamellae which lie parallel to the radii. Single crystals of PE have been obtained in a wide variety by cooling dilute solutions.

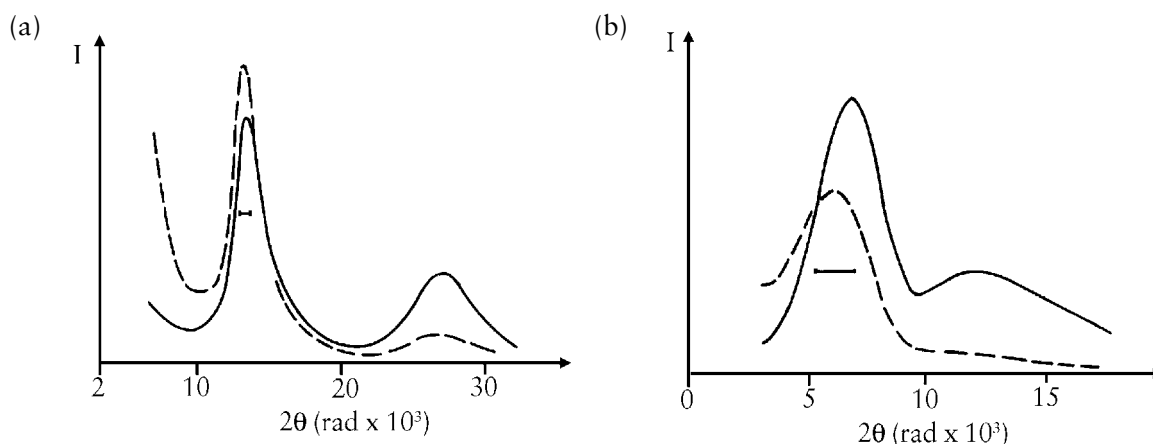


Figure 3.28 Small-angle X-ray scattering: (a) PE single-crystal mat; (b) annealed PE. Dashed lines: observed; solid lines: Lorentz corrected [30]

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3.18 Performance in Service [67]

3.18.1 Thermal and Oxidative Stability

Unstabilised PE oxidises in the presence of air, the rate of oxidation increasing with increasing temperature. Oxidation leads to embrittlement, surface cracking, discoloration, and loss of mechanical properties and clarity. High-temperature degradation is encountered during melt processing or in service, which is accelerated by contact with certain metals. All commercial grades of PE incorporate stabilisers that give protection against oxidation during processing and under service conditions. Primary antioxidants inhibit oxidation by combining with free radicals. Hindered phenols (for example, butylated hydroxytoluene, BHT) are commonly used. BHT is US Food and Drugs Administration (FDA) approved but it suffers from high-temperature volatility and oxidation in the presence of metal residues left from catalysts produces a yellow colour. High-molecular-weight phenols are suitable for high-temperature processing/service conditions.

Secondary antioxidants or peroxide decomposers such as phosphites and thioesters inhibit oxidation. They are usually combined with primary antioxidants to produce synergistic effects. Careful selection of suitable stabilisers is necessary for food contact applications. Interaction with light stabilisers and other additives must be considered during selection (see Chapter 4).

3.18.2 Stability to Sunlight and UV Radiation

Unstabilised PE very rapidly becomes brittle when exposed (prolonged exposure) to sunlight, caused mainly by UV radiation. Degradation is accompanied by marked deterioration in mechanical properties, gloss loss, and cracking.

Light stabilisers (photostabilisers) are chemical compounds that interfere in the physical and chemical processes of light-induced degradation. The service life of unprotected PE in the dark at 20 °C is 8–10 years, and that of stabilised or crosslinked PE in moderate climates is 15–20 years. In tropical climates the service life is only two to five years, even if the products (pipes, tubes) contain stabilisers (~2%); the lifetime of films is only three months.

There are four classes of light stabilisers having different modes of action. These are discussed next.

- (1) *UV absorbers* are added to provide protection against harmful UV radiation. They absorb the UV radiation and release the excess energy as heat. UV absorbers are carbon black, benzophenone derivatives, benzotriazoles, esters, and hindered amines. Thick parts are much more stable than thin parts, films, and sheets. Hindered amines function as free radical scavengers and thus also have an effect as thermal antioxidants. They are effective at very low concentrations, but can interact with other additives such as titanium dioxide, halogenated flame retardants, phenolic antioxidants, and pigments rendering them ineffective. The addition of stabilisers may make materials unsuitable for food applications because of leaching and migration. The reduction in molecular weight during UV exposure is more severe at surfaces. Stabilised grades are delivered with various degrees of stabilisation and they must be selected according to application requirements. A balance of stabilisation system and other additives together with homogeneous distribution are necessary to achieve optimum resistance to light, UV radiation, and weathering. Blooming and migration are secondary effects, which must be taken into consideration. Long-term outdoor testing (natural ageing) is the most accurate method to test the efficacy of stabilising systems, but accelerated ageing is generally used by means of weatherometers. HDPE offers better oxidation and UV resistance in comparison with other grades. Only a few light stabilisers are suitable for LDPE, because most of them are not compatible enough at the concentration required, so they bloom more or less rapidly. With the development of nickel quenchers, significant improvement of the light stability of LDPE has been achieved.
- (2) *Quenchers* confer stability through energy transfer. They are of the benzotriazole and benzophenone types. Certain nickel compounds are also used as quenchers, these being used exclusively for polyolefins.
- (3) *Hydroperoxide decomposers* play an important role in peroxide group decomposition. The most important are metal complexes of sulfur- and phosphorus-containing compounds such as dialkyldithiocarbamates and nickel alkyldithiocarbamates.
- (4) *Free radical scavengers* act by free radical scavenging reactions. HAS have the highest efficiency.

Combined formulations of light stabilisers and antioxidant systems are more effective in photostabilisation. The most efficient are combinations of nickel-containing light stabilisers and HAS with UV absorbers. Some application fields require the incorporation in LDPE films of certain fillers, for example, china clay, talc, and chalk. These fillers have a pronounced antagonistic effect on the light stability of the films, which is attributed mainly to transition metals present in the fillers as impurities. An increased concentration of light stabilisers is necessary in these cases.

3.18.3 Chemical Resistance

PE has outstanding chemical resistance. Non-polar solvents (such as hydrocarbons and chlorinated solvents) are more easily absorbed by PE than polar solvents (such as soaps, wetting agents, alcohols), causing swelling, softening, and surface crazing. PE is extremely resistant to inorganic environments, being unaffected by aqueous solutions of inorganic salts and mineral acids, even when concentrated. PE is attacked by oxidised agents such as chlorosulfuric acid, pure fuming, nitric, and sulfuric acids, and halogens. In formulations, stabilisers and other additives can be attacked by chemicals to which PE is resistant, so affecting the stability and properties of the PE material. Increasing temperature reduces the resistance to aggressive environments. The higher the degree of crystallinity of PE, the greater the chemical resistance. Homopolymers are also more resistant than copolymers.

3.18.4 Environmental Stress Cracking Resistance

Environmental stress cracking is the surface-initiated brittle fracture of a polymer under stress in contact with a medium in the absence of which fracture does not occur under the same conditions of stress. Combinations of internal and/or external stresses may be involved. The sensitising medium can be gaseous, liquid, or solid. PE products prematurely fail in the presence of detergents and other active environments. Many plastics suffer environmental stress cracking or embrittlement on prolonged contact with boiling detergent solutions. A reflux test involving 1000 hours in boiling detergent solution is used to measure water absorption, embrittlement, and change in dimensions.

The term environmental stress cracking was used first in the context of PE cable insulation. PE was reported to be unsatisfactory for cable use, and was found to crack severely on contact with methyl alcohol at room temperature.

The problem of environmental stress cracking can be an important one for many applications in the medical industry. These include medical laboratory equipment, caps, closures, and implant components.

Several important molecular parameters for optimising environmental stress cracking resistance (ESCR) in PE are:

- Molecular weight. The higher the molecular weight, the longer the polymer chains, resulting in more tie molecules as well as more effective tie-molecule entanglements.
- Comonomer content. Because they contain a small amount of comonomer, such as 1-butene or 1-hexene, MDPE and LDPE exhibit short branches that tend to inhibit crystallinity. A higher comonomer concentration results in better brittle fracture resistance, most likely because the portions of polymer chains with the longer branches (for example, 1-hexene or longer) do not enter the tightly packed lamellar lattice.
- Density/degree of crystallinity.
- Lamellar orientation.

In the long-term and under stress PE exhibits slow crack and brittle fracture in non-aggressive environments (e.g., air and water). This is of particular importance because PE is used extensively in applications that demand long-term durability (cable, pipe, landfill linings, geotextiles). At ambient temperature for 'high-quality' grades the transition to brittle failure will occur after many years under stress.

To maintain or optimise material quality, accelerated test methods are needed. Increasing the applied stress is not an option because it induces ductile failure. Increasing the test temperature is frequently used but this must be below 50 °C where morphological changes are induced (**Figure 3.29**). Certain chemical environments such as Igepal CO-630 (a nonylphenoxy polyethanol surfactant with solubility parameter of 20 MPa) have been found to accelerate the phenomenon, particularly when combined with elevated temperatures and notching. The cracking of PE in air or an active fluid is the consequence of micro-yielding, followed by fibrillation and cavitation, followed by fibril rupture. The activation energies of ductile and brittle failure are the same at 85.5 kJ/mol.

In blow moulded HDPE containers for storage and transport of alcohols for industrial use, although they were tested for chemical compatibility and ESCR, fracture initiated adjacent to one or both of the cap lugs. This coincides with the maximum tensile strength due to the screw torque and with the location of a rubber O-ring which was coated with grease (silicone) to lubricate the assembly.

Water treeing failure of XPE high-voltage power cable insulation was found to occur. Failure occurred after seven years of service and was caused by the growth of vented water trees when exposed to a moist environment. XPE also undergoes also degradation when exposed to sunlight.

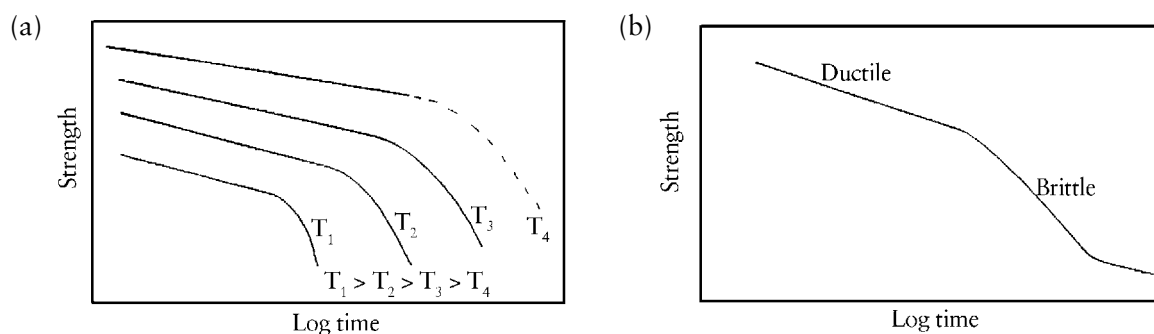


Figure 3.29 Ductile to brittle transition of PE as a function of temperature and time [67]

Reproduced with permission from D.C. Wright, Failure of Plastics and Rubber Products, Rapra Technology, Shrewsbury, UK, 2001. Copyright Rapra Technology, 2001.

Cellular LDPE with a dielectric constant less than 1.4 has been used successfully for many years to insulate high-speed communication wires and cables. Intranet systems for interoffice communication may employ hundreds of bundled wires. These are usually housed in metal conduits and trunking. Failure includes loss of links and corruption of data during transfer. This is because extensive cracking of the wire insulation can occur, caused by silicone oil.

As thermal insulation cover material, LDPE competes with polyvinyl chloride. Sometimes the covers disintegrate at the areas of contact with the highest temperature. Copper catalyses oxidative failure.

Failure of LDPE by photo-oxidation consists of discoloration, embrittlement, extensive circumferential microcracking, and brittle fracture.

In MDPE pressure irrigation pipe, carbon black is used to provide the necessary resistance to UV degradation. Such systems have an excellent record of good service. Spiders as essential support elements within a pipe extrusion die can act as stress concentrators. These and poor distributive mixing of the carbon masterbatch by the extruder can lead to a very poor resistance to UV degradation.

3.19 Permeability

3.19.1 Permeability to Water and Other Liquids

PE is virtually impermeable to water and aqueous solutions. It does not swell when immersed in water. The water vapour permeability of PE film is $1.0 \text{ g/m}^2/24 \text{ h}$ for HDPE and $5.0 \text{ g/m}^2/24 \text{ h}$ for LDPE. Changes in relative humidity have no effect on the properties of the material. Very slight water uptake can be determined when there is a temperature change in a hot, damp atmosphere due to surface adsorption. Fillers, reinforcements, and additives may slightly increase the water uptake (particularly products pigmented with carbon black). There is appreciable adsorption and permeation with certain organic solvents (non-polar solvents). The degree of permeation increases with temperature.

3.19.2 Permeability to Gases

HDPE has a better resistance to permeation by gases than LDPE (Table 3.22).

Table 3.22 Permeability to gases ($10^{-3} \text{ cm}^{-3} \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$) at 25 °C of various PE and copolymers

Polymer	Nitrogen	Oxygen	Water vapour	Carbon dioxide	Helium
HDPE	0.143	0.403	60; 12	0.36; 13	1.14
LDPE	0.969	2.88; 15	90; 420	12.6; 55	4.9
EVA	132	–	–	2800	59.2
EP	0.143–4.87	–	12–450	0.403	0.36

3.20 Crosslinking and Sterilisation

Radiation crosslinking of PE is a standard process for improving many material properties and in particular the resistance to creep at ambient and elevated temperatures. Typically, the material is modified in this manner by exposing it to a ‘saturation dose’ of γ -rays in the absence of air/oxygen. The dose ranges from 100 to 300 kGy depending upon the material grade and formulation. Up to the saturation dose, the crosslink density as measured by gel content (by xylene extraction) increases linearly with dose. Above this level, the gel content is independent of dose, suggesting a dynamic equilibrium between chain extension and chain scission. The saturation dose is increased by the action of antioxidants that stabilise macroalkyl radicals. It follows that antioxidants are (partly) consumed as a result. The saturation dose is decreased by the addition of radiation sensitisers, which include trifunctional monomers such as trimethylolpropane trimethacrylate and triallylcyanurate.

As PE is a popular material for disposable medical devices, considerable effort has been applied to assess its response to radiation sterilisation. In experiments up to 75 and 200 kGy, it has been reported that most mechanical properties improve with radiation exposure. Slight discoloration due to phenolic-based antioxidants and particularly in combination with HAS was one detrimental aspect observed. Radiation resistance is measured by changes in properties. Bulk properties such as HDT and failure by yielding will be insensitive to surface degradation and will therefore imply high radiation resistance. Tensile properties are less sensitive to surface degradation than flexural ones.

UHMWPE sterilised using γ -rays is used extensively in orthopaedics for artificial hip and knee components. In some designs, contact stresses approach the yield stress (~ 20 MPa) of the material. The changes in short-term mechanical properties of UHMWPE following exposure to γ -rays at a dose of 30 kGy are listed in Table 3.23. The effect on long-term properties and hence durability are more significant. Under reverse bending fatigue, there is little effect of radiation exposure up to 2 million cycles. Above this limit the effects of sterilisation become significant. At 10 million cycles, the fatigue strength is reduced from 31 MPa (unsterilised) to 18 MPa (sterilised).

Sterilisation of disposable articles is generally carried out with a radiation dose of about 25 kJ/kg or 25 kGy (2.5 Mrad). Due to the absence of tertiary carbon that initiates the degradation of the material and loss of mechanical properties, PE has a considerable radiation resistance.

Table 3.23 Effects of γ -ray (30 kGy) sterilisation on UHMWPE (GUR 415 from Hoechst)

Property	Unsterilised	Sterilised
Hardness (Shore D)	66	67
Compressive modulus (MPa)	538	677
Yield strength (MPa)	20	24
Ultimate tensile strength (MPa)	40	43
Elongation at break (%)	353	315
Impact strength (kJ/m ²)	107	86

XPE is an important material for cable insulation in nuclear installations. In air, at 100 kGy of radiation at low dose rates, the strain at break (259%) of XPE is unaffected. Above a dose of 100 kGy, strain at break declines significantly and is sensitive to dose rate because of high oxygen permeability within XPE.

3.21 Correlations Between Polyethylene Properties

The way in which some PE properties vary with density, MFR, and MWD is presented in Table 3.24.

Table 3.24 Correlations between PE properties with increase of density, MFR and MWD			
Property	Increase of density	Increase of MFR	Increase of MWD
Abrasion resistance	+	-	-
Barrier properties	+		
Blocking resistance	+	-	
Brittleness resistance	-	-	-
Brittleness temperature	-	+	-
Chemical resistance	+	-	
Cold flow resistance	+	-	+
Dielectric constant	+ (sl)		
Environmental stress cracking resistance	-	-	-
Gloss	+	+	
Hardness	+	- (sl)	
Haze	-	-	
Impact strength	-	-	-
Load-bearing properties, long-term	+	-	+
Melt elasticity		-	+
Melt extensibility		+	-
Melt shrinkage	-	-	
Melt strength		-	+
Melt viscosity		-	
Permeability	-	+ (sl)	
Refractive index	+ (sl)		
Shear stress, critical, for inlet fraction		+	-
Softening point	+		+
Specific heat	- (sl)		
Stiffness	+	- (sl)	
Tear stress of oriented film	-	-	
Tensile elongation at break	-	-	
Tensile modulus	+	- (sl)	
Tensile strength at break	+	-	
Tensile yield stress	+	- (sl)	
Thermal conductivity	+		
Thermal expansion	-		
Transparency	-	-	
Viscosity, rate of change with shear rate			+
+: increase -: decrease sl: slight increase/decrease			

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4 Additives

The reader is referred to Sections 3.18.1 and 3.18.2, which are also relevant to the discussion of additives.

The numerous and diverse applications of polyethylene (PE) would not be possible without the development of suitable additives. Additives are used for the preservation of some properties (stabilisation against the action of heat, oxygen, light, and so on), to facilitate the processing of different items, and/or for the modification of some properties for special purposes. Usually, the first two objectives must be considered and fulfilled concomitantly, and therefore complex systems of additives (antioxidants, light stabiliser mixtures, or complex formulations) are used. As PE degradation may occur at every stage, it is advisable to add some kind of stabilisation as early as possible, even in the polymerisation process, or to add the antioxidant before the polymer comes into contact with air. In drying, palletising, or processing operations the masterbatches are preferred as powder or as master fluff. Crosslinking agents are applied in phlegmatised form, pre-blended with mineral fillers or extender oil and sometimes with stabilisers. Such mixtures facilitate peroxide handling. Some additives used in PE formulations may play a multiple role sometimes they can even have a negative effect. For example, many pigments act as photostabilisers, the protective action against light being fulfilled by the coloured pigments, while white pigments such as the anatase form of titanium dioxide act as photosensitisers. The choice of a suitable additive for a particular use is very important, as it involves knowledge of the behaviour of each additive and its interaction with any other additives that may be present (Table 4.1).

Table 4.1 Common additives of ultra high molecular weight PE [1]

Property enhancement	Additive
Surface lubricity	Silicone oil, molybdenum disulfide, carbon black, graphite, polar waxes, vegetable oils, mineral oils
Abrasion resistance	Dicumyl peroxide
Surface hardness	Talc, hollow glass spheres, kaolin, short glass fibres, wood flour
UV resistance	Carbon black, hindered amine stabilisers (HAS)
Heat resistance	Metal flakes, phosphite-based stabilisers
Electrical conductivity	Carbon black, graphite, carbon fibres

4.1 Antioxidants, Inhibitors, or Heat Stabilisers

Antioxidants, inhibitors, or heat stabilisers ensure protection against thermal and oxidative degradation during processing and/or environmental exposure under service conditions. They are classified as chain transfer or primary antioxidants (sterically hindered phenols, secondary aromatic amines, aminophenols, aromatic nitro- and nitroso-compounds) and preventive or secondary antioxidants (organic phosphites and phosphonates, thioethers, thioalcohols, dithiocarbamates, mercaptobenzimidazoles, aminopyrazoles, metallic chelates). Antioxidants can be incorporated either during the manufacturing process of polymers or in the compounding step of mixtures. The efficiency of phenolic antioxidants depends on their structure. The efficiency of highly hindered phenols is similar to that of weakly hindered phenols, but the former do not confer colour to the products. The primary and secondary antioxidants for linear low-density PE (LLDPE) are the same as those for high-density PE (HDPE); however, incompatibility is more of a problem in the former case. Phosphorus-containing antioxidants do not ensure good stability of LLDPE, while polymeric hindered amine stabilisers (HAS) contribute markedly to an increase of LLDPE stability. Stabilisation of crosslinked PE is achieved using the same antioxidants as for non-crosslinked PE. If there is to be a direct contact with copper, the addition of a metal deactivator is mandatory.

Pentaerythritol-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] and octadecyl [3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] are highly effective, non-discolouring stabilisers for HDPE, LDPE, LLDPE, and EVA copolymers against thermo-oxidative degradation, even under severe conditions (300 °C). These additives can be used instead of thioesters that impart an unpleasant odour to PE. They are used as stabilisers for materials coming in direct contact with food as packaging films, various domestic appliances, and other consumer goods. They permit the production of highly transparent non-discolouring films of LDPE and have no adverse effect on printability. They are extremely effective for injection moulded and rotational moulded HDPE articles (containers, films, and so on). The recommended concentration is 0.05–0.2%.

2,2'-Thiodiethylbis-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] effectively stabilises HDPE and LDPE, having good compatibility and not affecting their colour. It is particularly suitable for use in carbon black loaded PE formulations such as LDPE wire and cable insulation and chemically crosslinked PE.

For LDPE and LLDPE, the current standard systems used are binary blends of high molecular weight di-*tert*-butyl phenols (AO-1/AO-2) and phosphates (P-1/P-2). New high-performance ternary blends involving lactones (L-1) together with traditional phenols and phosphates are utilised more and more for demanding applications.

For extremely colour-critical applications such as fibres, phenol-free stabilisation systems are provided by a combination of hindered amines (HAS-1 or HAS-2) used either with hydroxylamine (NOH) or with a mixture of lactone (L-1) and phosphite (P-1). Addition of phosphite improves the melt flow and reduces colour intensity.

Vitamin E based systems provide an alternative way to stabilise polyolefins instead of the current state-of-the-art stabilisers, also providing superior melt flow control at low concentration for special applications such as food, cosmetics, and medical packaging. They have low migration, high extraction resistance, very good organoleptic properties and gel suspension, and prolong the shelf life of products. They can also be cost-effective because of the very low concentrations used (100 ppm can match the melt flow control obtained with 1000 ppm of a traditional phenol/phosphite blend [2]). They have a positive public perception. Other natural compounds with antimicrobial activity and antioxidant effect (such as grapefruit seed extract) are being studied for use in food packaging films made from polyolefins.

Minerals such as talc, calcined clay, and silica are infrared absorbers. EVA copolymer film is highly transparent to UV radiation and has a natural infrared absorption at a wavelength of around 1 µm. It can thus be used to retain the heat developed within greenhouses.

4.2 Masterbatches

A new antifog masterbatch with high 30% additive [UV stabilisers, benzophenone, polymeric hindered amine light stabiliser (HALS), *N*-alkoxy HALS (NOR-HALS), nickel quenchers, calcined clay fillers, and light diffuser] level has been developed by Ciba for agricultural and greenhouse films from LDPE and EVA (>18 wt% VA), having high transparency. The nickel quenchers cause the film to have a typical green-yellow colour. HDPE with silicone (a dispersion of high molecular weight polydimethylsiloxane (PDMS) with and without silane-grafted PE) is used as a compatibiliser.

Phenolic antioxidants, phosphates, and zinc stearate as acid scavengers are used for processing and long-term stabilisation of HDPE film.

4.3 Antistatic Agents

Owing to its high electrical resistance, PE tends to accumulate electrostatic charge, as do other polymers. This is a disadvantage because dust can accumulate on articles, which is often undesirable. Furthermore, the possibility of sparks presents a hazard in applications where explosive fumes may be present.

Antistatic agents can be added either directly or in masterbatch form. During processing, traces of antistatic agent migrate to the surface of the moulding and form a moisture-absorbent, weakly conductive layer. This reduces the surface resistivity, thus allowing the faster dissipation of accumulated electrostatic charge. For useful antistatic properties, the surface resistivity needs to be in the range 10^9 – 10^{14} Ω/m^2 . The optimum antistatic effect is generally obtained after a storage period of about two or three weeks. In many cases the optimum effect is attained after only a few days, but under arid conditions it is reached very much later and is reduced. The antistatic effect persists for a considerable time and articles can be washed in water without any marked decrease in antistatic activity. Grades with low crystallinity allow faster migration of antistatic agents to the surface, thereby allowing the optimum performance to be reached quickly.

The incorporation of an antistatic agent has little or no effect on the mechanical, chemical, or thermal properties and no effect on the processing conditions. However, the presence of antistatic agents may affect the transparency and printability and may make PE non-compliant with US Food and Drug Administration (FDA) regulations, although FDA-approved antistatic agents are available.

With the inherent hygroscopic nature of antistatic agents, it is advisable to pre-dry the granules before processing. The exact amount of antistatic agent added depends on other property requirements such as transparency, FDA approval, printability, and compatibility with the polymer. Articles can also be coated with suitable antistatic agents. To a lesser extent, lubricants can also act as antistatic agents and *vice versa* by friction reduction. Typical applications where antistatic properties are required are household items, housing for electrical and electronic appliances, parts that undergo friction or sliding, and so on.

4.4 Electromagnetic/Radio Frequency Interference Shielding

In some cases electrostatic dissipation is required (semiconductor devices or when a product is used in a hazardous environment). In other cases shielding a component against electromagnetic or radio frequency interference is required. Many electronic and electrical devices, such as computers and mobile phones, emit signals that may interfere with communications. Plastic enclosures used to house these devices can eliminate or attenuate these signals. The high electrical strength, low dielectric constant, and low dissipation factor of PE do not indicate it as a good material for this purpose. Carbon black incorporation, metal deposition using metallising or electroplating, or adding metal fillers or nickel-coated graphite fibres are methods used to impart sufficient shielding capability of PE.

4.5 Antifogging Agents

Fogging occurs when water droplets formed from the exposure of the moisture in foods to low storage temperatures condense on the inside surface of packaging films. Use of polyglycerol ester in a sorbitan ester of a fatty acid has been reported for antifogging applications in refrigerator packaging. Glycerol monostearate is used for LLDPE film. Slip agents can also act as antifogging agents.

4.6 Biocides

Biocides inhibit bacterial growth. In traditional applications of PE the control of micro-organism growth is virtually non-existent. Their use is only for aesthetic and sanitary purposes.

4.7 Blowing Agents

Blowing agents can be physical and chemical. Physical blowing agents are low-boiling halogenated hydrocarbons (which are used in the presence of activators such as silica, silicates, and sulfides). Chemical blowing agents can be inorganic (ammonium carbonate, bicarbonate alkaliboronanhydride) or organic (azo compounds such as azodicarbonamide, hydrazine derivatives, semicarbazide, azoisobutyronitrile). Azodicarbonamide decomposes rapidly, being recommended for electrical cable insulation, while *p,p'*-oxybisbenzenesulfohydrazine with a high decomposition rate is preferred for the extrusion of parts with thick walls where the cooling is difficult. Through the addition of a suitable blowing agent, fine-celled foams with apparent density down to 0.5 g/cm³ can be produced by extrusion or injection moulding.

4.8 Biosensitisers and Photosensitisers

Biosensitisers and photosensitisers are used to obtain PE with predictable life times. Iron complexes Fe(III)-acetylacetonate, Fe(III)-2-hydroxy-methylacetophenoneoxime, transition metal (Co, Ni, Cr, Zn)-*N,N'*-diethyldiselenocarbamates or other metallic complexes, and blends with natural polymers (starch, cellulose, lignin, proteins) are mostly used.

4.9 Conducting Agents

Conducting agents reduce the specific resistance. Aluminium flakes coated with coupling agents, steel microfilaments, silvered glass fibres and spheres, carbon black, carbon fibres, and organic semiconductors are used.

4.10 Coupling Agents

Coupling agents such as neoalkoxy titanate or zirconate improve interfacial interaction and filler dispersion in composites.

4.11 Crosslinking Agents

Crosslinking agents are used in the vulcanisation of polyolefin rubbers and for crosslinking of PE and ethylene copolymers to improve the dimensional stability, control the melt flow index, and so on. Organic peroxides are frequently used in the presence of co-agents (ethylene glycol dimethacrylate, diallylterephthalate), photoinitiators, aromatic ketones, quinones, and so on. The mechanical properties generally deteriorate when the maximum quantity is exceeded. However, higher quantities than the minimum are necessary if the compound contains substances that can scavenge free radicals, for example, antioxidants or extender oils. The negative influence of these types of additives can be partially compensated for by the use of co-agents. Acidic fillers (talc, silicates) have a negative influence on crosslinking with peroxides due to the catalytic effect of the materials on the ionic decomposition of peroxides and to the adsorption of the crosslinking agents on the surfaces. This can be remedied by increasing the peroxide quantity and/or by the addition of co-agents. Although by radiation crosslinking it is possible to obtain materials free from the products of peroxide decomposition, this process requires a high level of capital expenditure and can only be used to a certain polymer depth. Crosslinking by peroxides is applied for PE and EVA copolymers used for cable and wire insulation, shoe soles, and so on.

4.12 Flame Retardants

PE is basically flammable and ignites at temperature below 600 °C, although its burning rate is slow. It continues to burn when the ignition source is removed and melts with burning drips. The

combustion temperature is 350 °C and the temperature of ignition is 360–367 °C. Combustion of PE is not accompanied by the evolution of environmental pollutants, but it produces small amounts of soot, without char formation.

Flame retardants are added to reduce the flammability of PE. The unmodified PE grades have a 94 horizontal burn rating up to 0.8 mm thickness. Suitable flame-retardant grades with V-O rating at 3.2 mm thickness are available from compounders. Flame retardants can reduce the processability and interfere with the function of certain hindered amines as light stabilisers. Flame-retardant grades are generally not suitable for use in food contact applications.

Flame retardants include halogen-containing compounds (which can cause problems), $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, phosphorus-containing organic compounds, antimony oxides, and boron compounds. Many inert fillers and additives, such as talc, CaCO_3 , crushed marbles, and clays, can also act as flame retardants or thermal skins. At high loads (>20 wt%) they lead to mass dilution and slow heat generation, favouring charring and reducing flammability and smoke generation. Smoke suppressants are also sometimes added. Antimony oxide is generally added together with halogenated flame retardants, which have a synergistic effect. $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ dissociate in the presence of heat to form water and metal oxides. The water dilutes the combustion gases and takes away the heat from the burning plastic, while the oxides form an insulating char layer on the burning plastic.

Unmodified PE has a limiting oxygen index (LOI) of 17, which is increased in the presence of flame retardants. Suitable flame-retardant grades must have a LOI of 28.

Fine-precipitate $\text{Al}(\text{OH})_3$, a low-smoke, halogen-free flame retardant, developed by Nabaltec GmbH, has good powder processing and compound properties. Chlorinated PE and chlorosulfonated PE are also used as flame retardants. $\text{Al}(\text{OH})_3$, in particular, is used in cable insulation made from LDPE and HDPE and roof films are made from flame-retarded PE.

Flame retardants are reactive compounds, which means that they are often less stable than the polymers in which they are used and they may decompose during normal processing and/or use. This limits the choice of additives that can be used. They are particulate fillers. Large amounts are necessary in PE, they are difficult to disperse uniformly, and they result in serious stiffening and even embrittlement. Organic halogen plus antimony oxide compounds are the most frequently used types of flame retardant. They can produce high LOI and achieve UL-94 V-0 ratings, and they generally reduce smoke. However, they produce gases that are toxic and corrosive.

4.13 Fillers and Reinforcements

Fillers and reinforcements are solid additives that differ from the plastic matrices by their composition and structure. Inert fillers or extenders increase the bulk, solve some processing problems, and reduce costs (by increasing thermal conductivity they improve production rates). Active fillers and reinforcements produce specific improvements of certain mechanical or physical properties, including modulus, tensile and impact strength, dimensional stability, heat resistance, and electrical properties. Fillers and reinforcements suitable for PE include: natural and precipitated calcium carbonate, talc, mica, silica and silicates, metal powders, kaolin, carbon black, aluminium trihydrate, wallastonite, wood flour, asbestos, glass spheres, glass fibres, reinforcing fibres, and so on. Carbon fibres, graphite, whiskers, and so on are also used.

4.14 Slip and Antiblocking Agents

To decrease the friction of films in contact with processing and conversion equipment, a lubricating agent known as a slip agent is added. Slip agents migrate to the surface and reduce the coefficient of friction, allowing for faster line speeds (lubrication). Primary amides, secondary amides, and ethylene

bisamides are commonly used as slip agents. They should not interfere with corona treatment or printing and should not have a deleterious effect on the clarity of films.

Blocking is a term describing a polymer film sticking to itself as a result of it being in roll form. Antiblocking agents are added to overcome this problem. Typical antiblocking agents are silica, talc, and diatomaceous earth, which are not miscible with polymers migrating to the surface. Addition of just the right amount and good dispersion are the critical factors to avoid the formation of microscopic roughness on an otherwise smooth film surface. They are especially used for LDPE heavy-duty sacks.

4.15 Metal Deactivators and Acid Scavengers

Metal deactivators and acid scavengers retard metal-catalysed reactions. They are chelating agents that effectively retard metal-catalysed oxidation. Metal deactivators are used to deactivate metal residues present in formulations due to catalyst residues, impurities in additives, direct contact with copper in wire and cable applications, and metal inserts.

Metals (copper and copper alloys, nickel, iron) have a strong adverse effect on PE because they accelerate degradation. Metal deactivators (organic molecules containing heteroatoms or functional groups such as hydroxyl or carboxyl) act by chelation of the metal to form inactive or stable complexes. The concentration used is about 1%. Acid scavengers (or antiacids) are used to neutralise acidic catalyst residues. Calcium or zinc stearate are commonly used, and also function as internal lubricants. Inserts should be made of light metal or be nickel or chromium plated.

4.16 Nucleating Agents

Nucleating agents modify the crystallinity and crystal structure, which results in less scattering of light. This technique is used in injection moulding to improve clarity and rigidity. The crystallites in clarifier-containing grades are much smaller than the wavelength of visible light, scattering is reduced, and the clarity is greatly improved. Nucleating agents are generally organic in nature, they melt during normal processing and thus become completely and evenly distributed in the resin. Pigments and residual monomers can also act as nucleating agents.

Nucleating polymers have a finer grain structure, which is reflected in their physicochemical characteristics, such as reduced brittleness, improved optical properties, greater transparency or translucency, high degree of crystallinity, and increased hardness, elasticity modulus, tensile strength and yield point, elongation at break, and impact strength. During processing, short cycle times are achieved, and after-crystallisation is prevented so that after-shrinkage of finished articles on prolonged storage is diminished. Nucleated PE films have reduced haze, higher gloss, and improved clarity.

Because HDPE has a high crystal growth rate, it is very difficult to nucleate. However, some moderately effective nucleating agents have been used, such as potassium stearate, benzoic acid, sodium benzoate, salts of mono- or polycarboxylic acids (for example, sodium succinate, sodium glutarate, sodium cyanamate), talc, and sodium carbonate [3, 4]. The latter increases the crystallisation rate and the crystallinity, so that the morphology of moulded parts is more uniform and the polymers have a better environmental stress crack resistance. Potassium stearate reduces almost five-fold the average spherulite size. In contrast to HDPE, LLDPE is easier to nucleate because the incorporated comonomers reduce the crystal growth rate. LLDPE containing 0.2% *p*-methylidibenzylidene exhibits excellent optical properties (haze is 2.6% *versus* 12% for non-nucleated films). Epitaxial crystallisation on other polymer substrates has also been applied.

4.17 Pigments and Colorants

Many materials are commercialised in coloured form, colour increasing the attractiveness of the final product. Colour change is a selective wavelength dependent absorption and/or light scattering (reflectance). Dyes can only absorb light and not scatter it, the products being transparent. The optical effect of pigments is different: reflectance of light takes place, the article becoming opaque and coloured if the absorption is selective. There are fluorescent whitening agents, nacreous pigments used in HDPE and LDPE bottles to increase brilliance, metallic flakes, and inorganic and organic pigments and colorants.

4.18 Additives Used for Polyethylene Fibre Production

The use of additives in PE fibres can be divided into three categories:

1. Polymer stabilisation during manufacture.
2. Coloration through polymer modification or dye-receptor addition before extrusion or by adding dye to the melt. Films, fibres, and tapes are coloured almost exclusively with concentrate granules, the amount of which varies between 1 and 10% in correlation with the depth of the shade required, thickness and opacity, fastness to light, rubbing, and washing.
3. Fibre finishing (surface coating) for the improvement of textile processability, handling, soiling properties, antistatic properties, slip and stick behaviour, lustre, degree of whiteness, shrinkage, splitting tendency, flammability, and mechanical and chemical properties.

Stabilisers, metal deactivators, dye-receptors, whiteners, and nucleation agents are incorporated to a certain extent by raw material producers, while stabilisers, antistatic agents, flame retardants, and masterbatches of pigments are incorporated by fibre producers. Lubricants and softening agents as well as preparations for mechanical spinning and weaving are applied during textile processing. The use of masterbatches prepared by melt mixing produces an extremely homogeneous blend but this has the disadvantage of polymer degradation due to the double thermal stress. Mechanical blending is used when the extruder is equipped with a static or dynamic mixer.

4.19 Other Additives

Processing enhancers include mineral oils, glycerol monostearate, and pentaerythritol monooleate. These decrease melt viscosity and/or elasticity at low shear rate and result in shorter cycle times without sacrificing peak impact strength. Ultrafine monospherical silica particles and boron nitride are also used as additives for special purposes because of their high-performance mechanical properties. Combinations of liquid polybutadienes (with and without functional groups) and dialkyl peroxide have been developed as compatibilisers for polyolefin blends (LLDPE/HDPE/polypropylene).

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5 Rheological Behaviour

The flow properties of molten polyethylene (PE) are of primary practical concern in forming, moulding, or extrusion processes. Deviating considerably from ideal Newtonian flow, melts of PE show non-ideal viscoelastic behaviour; their shear rate *versus* shear stress plot is non-linear. Very closely related to this non-linear behaviour of pseudoelastic materials is their elastic nature, in that some recovery may be observed when an applied stress is relaxed. Molecularly, chain disentanglement in the course of increasing stress can explain these phenomena.

Melt fracture, another phenomenon typical of PE melts, occurs on extrusion through a capillary die at high shear rates, resulting in an irregular and rough extrudate. The critical shear rate or stress is that at which a rough surface is first observed. Since this irregularity increases with increasing extrusion rate, it poses limitations on processing rates and requires control in the manufacture of sheet and film.

Rheological properties can be evaluated from the data obtained using rotational rheometers, which are of two types: the rotating cylinder and the rotating flat disc or cone. Rheological parameters may be calculated from measurements of torque, speed of rotation, and the approximate geometrical dimensions of the system. A device for measuring the processability is the Brabender Plastograph, which measures the torque required to mix a molten resin in a heated chamber by dual mixing blades. The equilibrium torque is a measure of processability. Stability can be measured by the decrease of equilibrium torque as a function of milling time, while the variation in torque over short periods of time is believed to be related to the elasticity of a sample. In the case of high-density PE (HDPE), melt viscosity increases (or melt flow rate (MFR) decreases) with increasing molecular weight of the polymer. A broadening of the molecular weight distribution (MWD) increases the dependence of viscosity on shear rate. In the case of branched PE, the dependence of melt viscosity on short-chain branching is quite minor compared to that on long-chain branching (LCB). The reduced viscosity observed for branched PE at constant molecular weight may be explained by the likelihood of increased coordination of the movements of the segments of flow.

5.1 Molar Mass Effects

For a technical polymer, the molar mass distribution (MMD) is a direct result of the statistics of the polymerisation process. In the process itself, it results from:

- the nature of the catalyst;
- the design and operational mode of the polymerisation reactor; and
- the monomer composition and feed mode.

In contrast to polypropylene (PP), for which degradation with peroxides in the molten state leads to a polymer with a significantly more narrow MMD, the peroxide treatment of PE-based systems normally results in branching and crosslinking reactions, with an increase of the average molar mass and broadening of the MWD. These different consequences of radical reactions in the polymer have to be taken into account when planning or analysing reactive modification processes.

For both PE and PP degradation processes are possible. The reaction to free radicals, in the case of PE, is strongly dependent on the catalyst type. For chromium-based catalysts branching is normally predominant, while for titanium-based catalysts degradation is more important.

As a result of all these possibilities, the shape and moments of the MWD can be varied over a wide range. In principle, correlations with all rheological properties are possible from the MWD if all chains are fully linear.

Many researchers have investigated the problem of interconversion between linear viscoelastic data and the MWD of a polymer. The most used parameter correlations involve the zero shear viscosity, η_0 , even if this is difficult to determine in the case of a wide MWD. Hence, a number of other parameters have been defined by industrial rheologists, which are related to the polydispersity (defined as the ratio of weight average to number average molecular weight, M_w/M_n). Steeman used numerical calculated rheological data based on model MWD to evaluate the applicability and limits of such quantities [1]. The correlations between M_w and η_0 were found to depend strongly on the polydispersity, as well as on higher moments of the MWD. No simple relationship could be established for the equilibrium compliance, $J_{e,0}$, for which different formulations have been tested. Examples of the results obtained are shown in Figure 5.1, where the asymmetry parameter $H = (M_z/M_w)/(M_w/M_n)$ is varied and a double reptation model is used for calculating the linear-viscoelastic material functions from the simulated MWD.

Another possible way to determine MWD-related parameters is the application of generalised Newtonian flow models for the viscosity curve $\eta(\dot{\gamma})$.

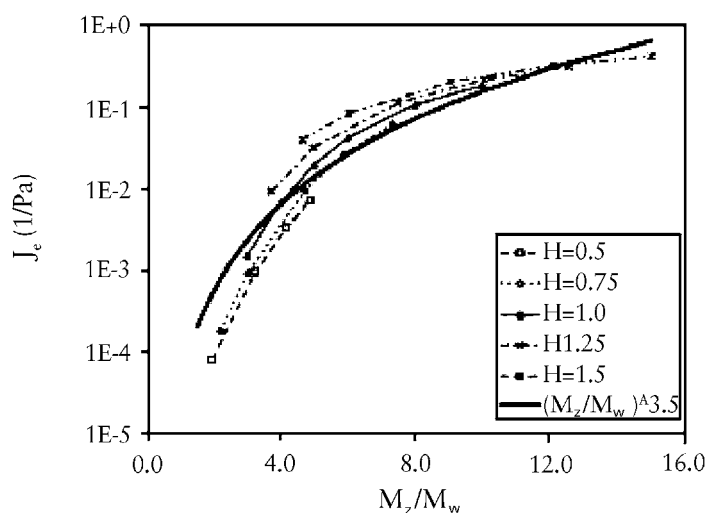


Figure 5.1 Steady-state compliance of model polymers plotted as a function of M_z/M_w , the solid curve indicates the dependence proposed by Kurata [1]

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5.2 Steady Flow Rheological Properties

Steady flow rheological properties refer to shear stress–shear rate dependence, zero shear (zero-limiting) viscosity (η_0), apparent (melt) shear viscosity (η), temperature-invariant dependence of melt viscosity (η/η_0), viscosity in elongational flow, critical shear rate ($\dot{\gamma}_0$) and critical shear stress, die swell, activation energy of flow, and melt flow index (MFI) or MFR and their dependences on different factors, such as shear stress, shear rate, LCB content, molecular weight, extrusion pressure, and temperature (Table 5.1 and Figures 5.2–5.5). Activation energy varies between 10 and 90 kJ/mol depending on PE type, molecular weight, and carbon number in side chains. All these dependences are important both in processing and utilisation of the materials.

5.2.1 Melt Flow Rate or Melt Flow Index

The processing technique basically decides the selection of MFR without loss of mechanical and thermal properties. A low MFR is preferred for techniques requiring a self-supporting melt such

Pressure (MPa)	Shear stress (MPa)	Shear rate (per s)	Average density (g/cm ³)	MFR (g/min)	Die swell ratio	Extrudate appearance
5.9	0.132	133.3	0.761	0.2854	1.74	Smooth
6.0	0.135	142.3	0.761	0.3052	1.75	Smooth
7.0	0.158	196.4	0.768	0.4250	1.80	Smooth
10.3	0.231	486.8	0.773	1.0596	–	Smooth
13.4	0.301	907.1	0.780	1.9926	2.14	Smooth
13.9	0.311	2467.6	0.780	5.4233	–	Rough
14.3	0.320	1053.7	0.779	2.3115	2.18	Smooth
14.6	0.328	3643.4	0.777	5.7774	–	Rough
14.8	0.331	1174.1	0.780	2.5811	–	Smooth
14.8	0.331	1170.1	0.777	2.5592	2.20	Rough
15.8	0.338	1267.8	0.772	1.7571	–	Wavy
16.1	0.344	1272.0	0.781	2.8010	–	Smooth

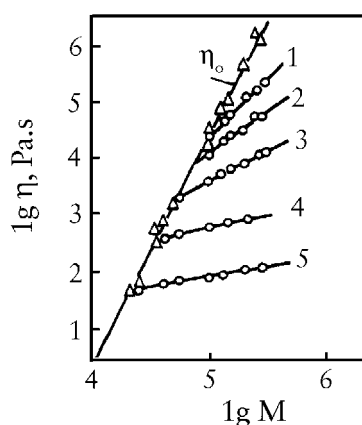


Figure 5.2 Viscosity of LHDPE at 190 °C *versus* molecular weight for different shear rates.
1: 1/s; 2: 10/s; 3: 10²/s; 4: 10³/s; 5: 10⁴/s [2]

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as film blowing, while a high MFR is needed for thin-wall injection moulding, film casting, and fibre spinning. A MFR of 0.5–2 g/10 min is chosen for pipes, sheets, and blow moulding, while a MFR of 2–8 g/10 min is used for films and fibre applications, and a MFR of > 8 g/10 min is used for extrusion coating, injection moulding, and fibre spinning. A higher MFR means low toughness whereas an adequate processability is obtained with a MFR which is as low as possible. Molecular weight and MWD are closely related to MFR.

5.2.2 Viscosity versus Shear Rate

It is possible for two materials with the same MFR to behave completely differently during moulding, as shear stresses are different from those used in MFR determination where low shear rates are used. Owing to the higher shear rates encountered in injection moulding, MFR is not a reliable measurement for the mouldability.

Viscosity *versus* shear rate or shear stress curves can be obtained using a capillary rheometer. These curves are useful because the behaviour during most melt processing operations (such as compression moulding, extrusion, and injection moulding) can be appreciated. The shear rates generated during compression moulding are quite low, while injection moulding generates very high shear rates. Shear rates during extrusion fall between these two. When the shear stress or shear strain on the material is increased, the viscosity of the melt decreases. The viscosity *versus* shear rate for different PE is compared in Figure 5.3.

PE grades with a wide MWD respond the most to an increase of the shear rate; these materials are processed more easily during injection moulding since the low molecular weight chains act as plasticisers. Narrow MWD grades are preferred for extrusion applications. In injection moulding processing the material is sheared between two surfaces, and hence shear viscosity is more important. Extensional flow and melt strength are useful during thermoforming, extrusion coating, foaming, blow moulding, and film blowing.

High melt-strength grades have a broader MWD and show greater shear thinning. These grades offer significant advantages over conventional grades for many processing routes: improved sag resistance and part uniformity for thermoforming, improved fine cell structure for low-density foams, and improved sag resistance, part uniformity, and bubble stability for blow moulding. The main use of the viscosity *versus* shear rate data is during the mould design to predict the behaviour of the mould during an actual filling cycle.

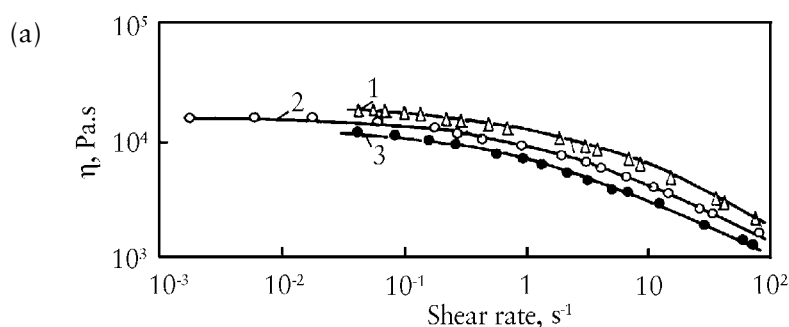


Figure 5.3 (a) Viscosity *versus* shear rate for LLDPE at different temperatures. 1: 160 °C; 2: 180 °C; 3: 200 °C

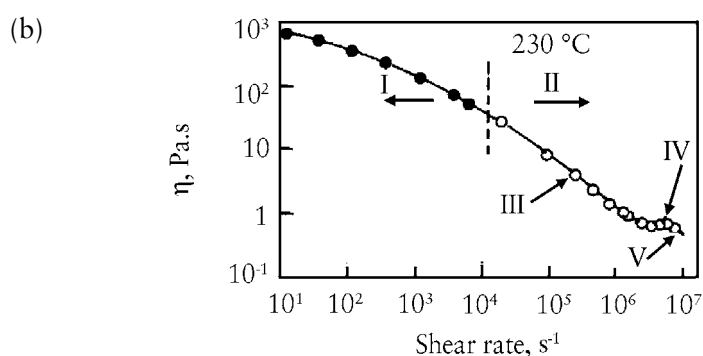


Figure 5.3 (b) Apparent viscosity *versus* apparent shear rate for HDPE at 230 °C ($L_d/D = 40$). I: Instron capillary rheometer; II: specially designed capillary rheometer; III: first non-Newtonian region; IV: second Newtonian region; V: second non-Newtonian region [2]

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The final choice of the grades for injection moulding from different equivalent grades available may be made from the injection pressure *versus* injection time curve for different grades. The material that offers the lowest injection time at minimum injection pressure would be a candidate for the final choice. In blown film applications, screw speed, power required, and head pressure estimation based on rheological characterisation may be useful.

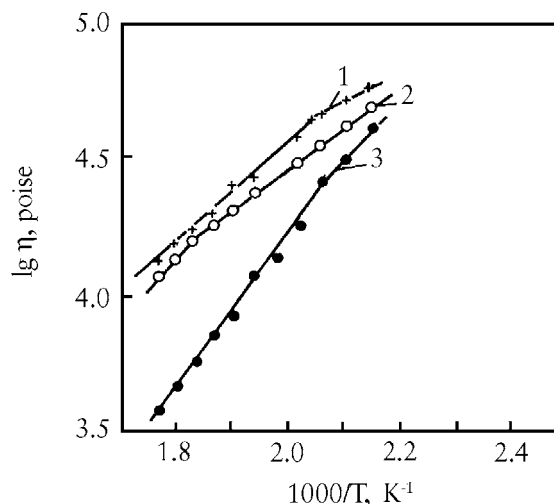


Figure 5.4 Viscosity dependence on temperature at shear stress $\tau = 50,000$ Pa. 1: HDPE; 2: LLDPE; 3: LDPE [2]

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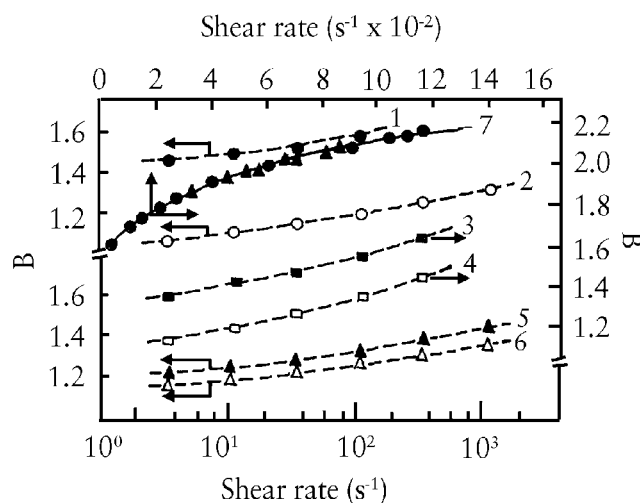


Figure 5.5 Die swell ratio (B) of HDPE (Marlex 6009) as a function of apparent shear rate (curve 7). ● constant pressure; ▲ constant speed. Die swell behaviour of LDPE with different shearing histories: 1 (●), 3 (■), 5 (▲): swell ratios of solvent-treated materials measured with a capillary ($L_d/D = 59.83$); 2 (○), 4 (□), 6 (△): swell ratios of full sheared materials measured with a capillary ($L_d/D = 59.83$). Temperature (°C): 1, 2: 190; 3, 4: 160; 5, 6: 130. MFI (g/10 min): 1, 2: 0.6; 3, 4: 8.1; 5, 6: 24. Density (g/cm³): 1, 2: 0.919; 3, 4: 0.911; 5, 6: 0.928. \bar{M}_n ($\times 10^{-5}$): 1, 2: 5.31; 3, 4: 3.35; 5, 6: 0.67. \bar{M}_w/\bar{M}_n : 1, 2: 17.0; 3, 4: 27.7; 5, 6: 7.4 [3]

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The dependence of the shear stress on shear rate is shown in Figures 5.6 and 5.7 for HDPE and LDPE, respectively.

The activation energy values are 25–30 kJ/mol in the temperature range 157–277 °C and 30–60 kJ/mol in the temperature range 127–227 °C for HDPE and LDPE, respectively.

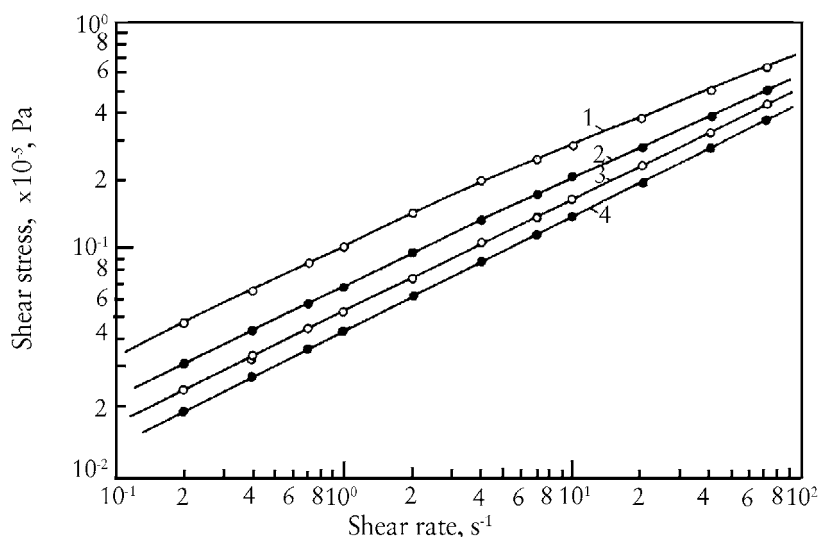


Figure 5.6 Dependence of shear stress on shear rate for HDPE at different temperatures. ($\rho = 0.942 \text{ g/cm}^3$, MFI = 2.21 g/10 min). 1: 150 °C; 2: 170 °C; 3: 190 °C; 4: 210 °C [2].

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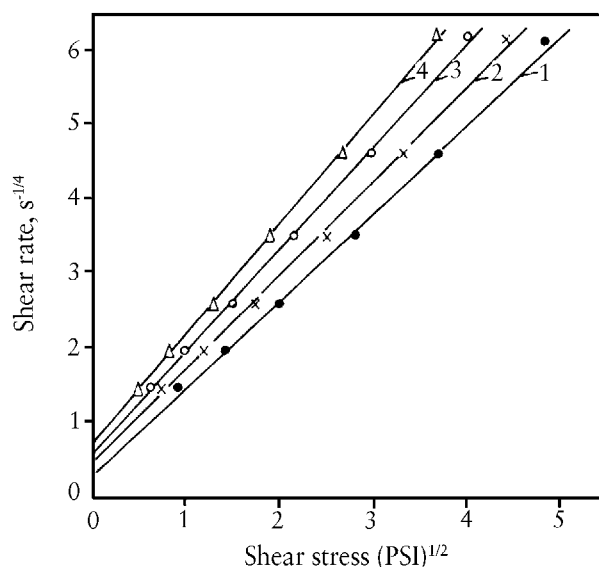


Figure 5.7 Dependence of shear rate on shear stress for LDPE (Dow 748) at different temperatures. 1: 190 °C; 2: 210 °C; 3: 230 °C; 4: 250 °C [2]

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5.3 Dynamic Rheological Properties

Dynamic rheological properties are dynamic viscosity and dynamic modulus. They depend on frequency, shear rate, time, and temperature. The parameters generally used are complex dynamic viscosity (η^*) and its viscous (η') and elastic (η'') components, and shear relaxation modulus (G^*) and its storage modulus (G') and loss modulus (G'') components (Figures 5.8). G' for LDPE has the highest value, and G' for LLDPE and mPE are very similar. The study of $\tan \delta = \eta''/\eta'$ is of great interest for processing.

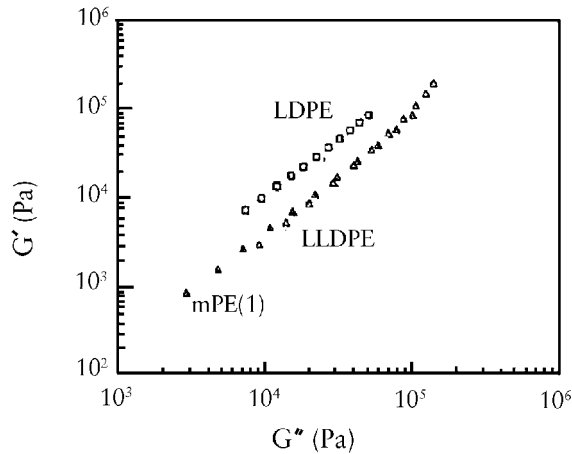


Figure 5.8 (a) Storage modulus *versus* loss modulus at a frequency of 1 Hz and temperature of 190 °C for three PE with similar MFR and different structure. □: LDPE; ▲: mPE(1); △: LLDPE [4]

Redrawn from L.O. Han and M.S. Jhon, Journal of Applied Polymer Science, 1986, 32, 3809

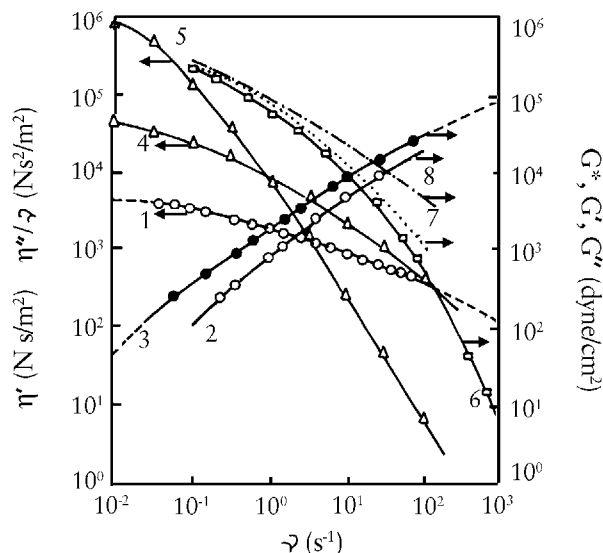


Figure 5.8 (b) Dynamic viscosity, dynamic modulus, and shear relaxation modulus *versus* frequency for different types of polyethylene. 1: HDPE: η' (ν); 2: HDPE, G' (ν); 3: HDPE, G'' (ν); 4: LDPE, η' (ν); 5: LDPE, $\eta'/\nu(\nu)$; 6: LDPE, $G^*(1/\nu)$; 7: LDPE, G' ($1/\nu$); 8: LDPE, G'' ($1/\nu$) [2]

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A shear history reduces the melt strength and the oscillatory shear modulus. This phenomenon is not caused by a decrease in the molecular weight, which remains the same as the original, indicating the absence of mechanical/thermal degradation during processing. The origin of ‘shear modification’ is generally considered to be the disentanglement of temporary couplings, especially those associated with long-chain branches. Specific processing histories, the processability and the quality of the resulting products affect to differing degrees. For example, a film obtained after sufficient processing has reduced surface roughness and results in a film of high transparency. Annealing of melt-processed samples enhances both the melt strength and the oscillatory modulus to the values of the original, unsheared samples.

5.4 Chain Structure Effects

5.4.1 Linear Chains

For PE, where stereochemistry does not play any role, the local structure is only affected by copolymers acting as very short-chain branches. Studying the effect of comonomers on the rheology of LLDPE-type polymers, it is found that while the comonomer has a certain effect on rheology (especially concerning the relationship between MWD and viscoelasticity), significant changes (such as the appearance of strain hardening) are observed only in the case of long side chains. These changes appear frequently when single-site catalysts are used. Such materials are directed at application areas presently covered by LLDPE/LDPE blends, because of melt strength requirements, e.g., in the blow moulding of large containers or film blowing.

5.4.2 Branched Chains

Polymers with LCB exhibit a completely different rheological behaviour, which has been formulated in the ‘pom-pom’ viscoelastic model, based on a phased reptation process of the side and backbone chains of the system. This model has been tested against the behaviour of different LDPE types, where shear and extensional viscosity are taken into account (Figure 5.9).

Apart from a change in the viscosity curve and the linear–viscoelastic behaviour in shear, which is presented schematically in Figure 5.10, the material behaviour in extensional flow is completely altered. In a transient experiment, strain-hardening effects are observed, resulting from an increased resistance of the material to disentanglement. For film blowing, blow moulding of large containers,

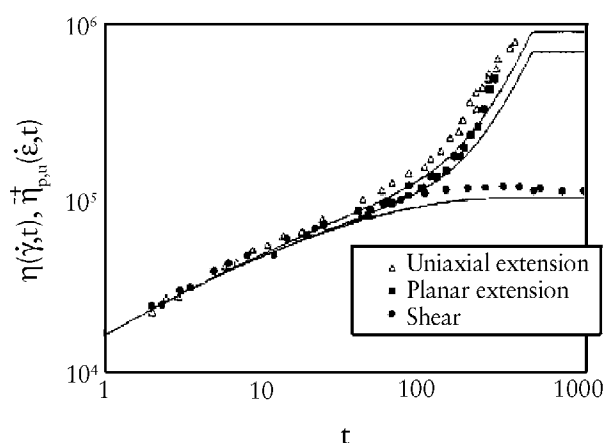


Figure 5.9 Transient uniaxial extensional (Δ), planar extensional (\blacksquare), and shear viscosity (\bullet) of an 11-mode pom-pom melt in start-up compared with measurement results for LDPE (shear/elongation rate, 0.01/s; temperature, 140 °C) [5]

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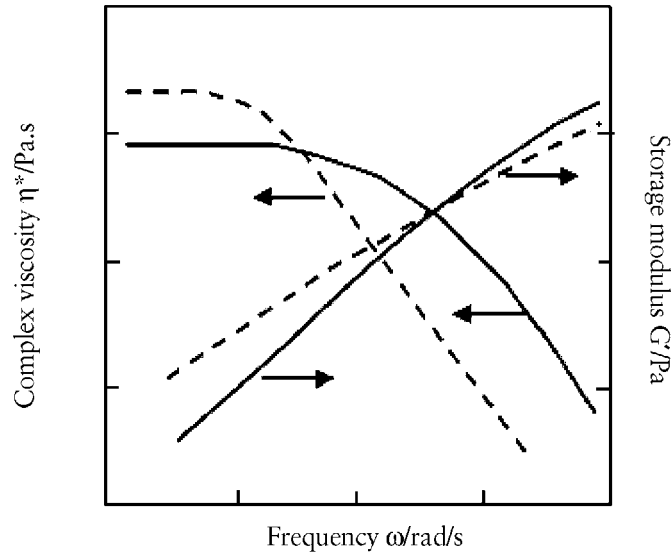


Figure 5.10 Schematic representation of the change of the viscosity and storage modulus curves with LCB. Linear polymer (solid lines), LCB polymer (dashed lines) [5]

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foaming, and so on, this is of great importance for processing behaviour. The extent and strain dependence of this effect is determined by both composition and branching distribution effects.

LCB polymers normally show a distinct dependence on their flow histories, a behaviour that is used for shear modification of LDPE.

Changes in the rheological behaviour of LDPE, caused by extrusion, occur without any change in the MWD. Such changes are not very evident for a bimodal HDPE. Changes induced by shear modification are also reflected in the die swell, as shown in **Figure 5.11** (the results for which were obtained for a technical LDPE sample (over-stabilised with antioxidant), which was sheared in a Brabender twin-blade kneader for different times). Theoretically, this process can be used for improving the processing behaviour and the product quality, especially surface smoothness and transparency. The reduction of the melt elasticity leads to a higher critical shear stress and less melt fracture, allowing for an output increase in conversion processes.

In general, various processing effects are induced by LCB. For example, in the case of PE and PP, the reduction of melt fracture by addition of LCB fractions is observed. For both polymers, the MWD plays an important role in defining the sensitivity of the material to melt fracture, while a certain amount of melt elasticity appears to be required for stable extrusion; however, too much melt elasticity becomes detrimental. In order to overcome this situation, hyperbranched processing aids can be added to boost the upper limit of processing speed in film extrusion. Other technical solutions involve die coating or the addition of fluorinated polymers as processing aids (this latter one being successfully used in the case of HDPE).

Branching effects are also recognised in shear flow, where LCB leads to an increased slope of the viscosity curve at comparable MWD (see **Figure 5.10**). Such measurements and conventional dynamic rheometry can be used for the determination of the activation energy from the zero shear viscosity or shift factor values, demonstrating a significantly higher temperature dependence of the viscoelastic material functions for branched systems. The results presented in **Table 5.2**, giving shift factors (a_T) and activation energies calculated from an Arrhenius-type temperature dependence, give evidence that this fact is true for both PE and PP.

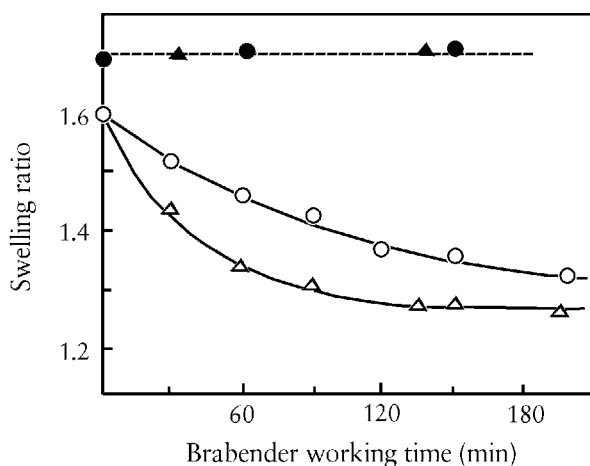


Figure 5.11 Effect of shearing in a twin-blade kneader on the die swell of an LDPE melt. (MFR (190 °C/5 kg) = 8.1 g/10 min; density = 0.914 g/cm³). O: Brabender shearing at 130 °C; Δ: Brabender shearing at 190 °C; ●, ▲: same conditions after solvent treatment of LDPE [5]

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LLDPE grades based on metallocene (mC) or single-site catalysts (SSC) can show a certain effect of LCB. This is because mC catalysts are able to incorporate vinyl-terminated chains as comonomers. This is considered as a possible way to improve the processing behaviour of these narrow MWD materials. The catalyst system used as well as the polymerisation conditions play an important role in the amount of LCB reached in the final product. **Figure 5.12** compares two different mC - LLDPE with and without LCB.

While the actual comonomer content dominating the density of the resulting materials is found to have very little effect on the rheology, the catalyst type determines whether predominantly linear or branched structures are produced.

5.5 Multiphase Systems: Inhomogeneous Products

Inhomogeneities in a material can be clearly seen from the rheological behaviour. Some negative effects of inhomogeneities include processing problems, such as surface distortion and even melt fracture, as well as a significant deterioration of the mechanical and optical performance of products.

Table 5.2 Shift factors for time/temperature superposition determined from dynamic moduli measurements in plate/plate geometry and activation energies calculated from an Arrhenius plot for LDPE, HDPE, and PP					
LDPE		HDPE		PP	
a_T	T (°C)	a_T	T (°C)	a_T	T (°C)
0.676	210	0.890	210	0.657	240
1.000	200	1.000	200	1.000	220
1.480	190	1.191	190	1.504	200
$E_a = 72.9$ kJ/mol		$E_a = 27.1$ kJ/mol		$E_a = 41.8$ kJ/mol	
$a_T = \exp[k(T - T_0)],$ where $k = E_a/R$					

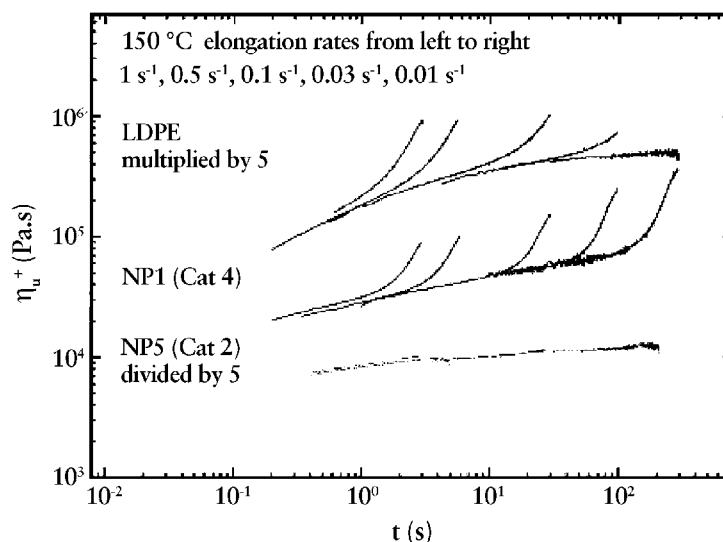


Figure 5.12 Time dependence of the elongational viscosity in uniaxial extension at 150 °C for two single-site LLDPE compared with a conventional LDPE. The catalysts are $[n\text{-butyl-Cp}]_2\text{ZrCl}_2$ (Cat 2) and $\text{CH}_3\text{CH}_2(\text{Ind})_2\text{ZrCl}_2$ (Cat 4) [5]

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An important practical aspect is the fact that inhomogeneity can be the cause of the appearance of so-called ‘gels’ in both PE and PP films. These ‘gels’ can result from the polymer itself, from decomposition products, and from non-polymeric impurities, for example, additive agglomerates or dirt particles from the production environment, such as cellulose fibres from bags.

The dissolution of high molar mass domains (polymer-based gels) for a bimodal HDPE during homogenisation in a Brabender-type two-paddle kneader is shown in **Figure 5.13**. It can be clearly seen that only after going through a maximum in energy uptake is homogeneity achieved.

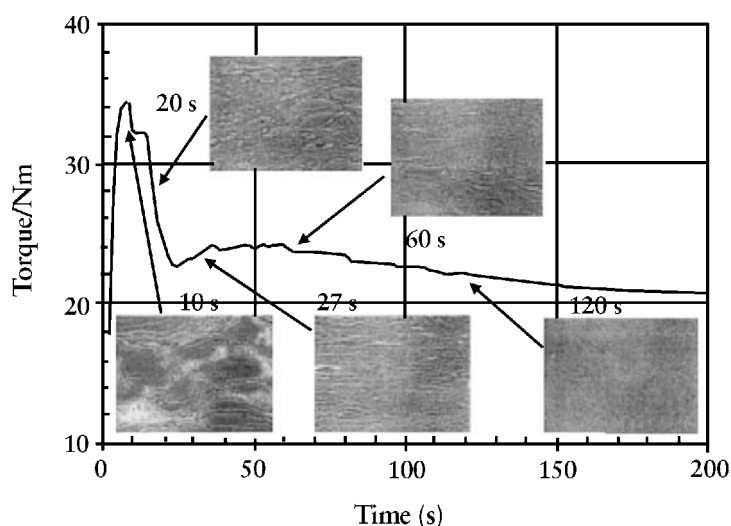


Figure 5.13 Homogenisation of a bimodal HDPE in a twin-blade kneader. Torque curve as a function of time and optical micrographs (magnification $\times 100$) of samples taken at different mixing times [5]

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6 Processing of Polyethylene

Polyethylene (PE) can be processed by all known processing operations, including injection moulding, extrusion (fibre and filament), compression moulding, blow moulding, thermoforming, rotational moulding and transfer moulding, casting, sintering and coating, and orientation.

Injection moulding is used for PE with a high melt flow rate (MFR) (low viscosity) and narrow molecular weight distribution (MWD). The viscous resin is squirted by a means of a plunger out of a heated cylinder into a water-chilled mould, where it is cooled before removal. Processing is performed from around 170 to 300 °C, depending on the material, but all types begin to decompose above 310 °C (and very short processing times are required beyond this temperature). PE does undergo some degree of shrinkage during injection moulding (low-density PE (LDPE) 1.5–3% and high-density PE (HDPE) 2–4%). Injection moulding is used to produce a wide variety of domestic and industrial items, which are too numerous to be listed in full.

Extrusion is the process by which melted PE is extruded at 160–240 °C to produce pipes using single- or twin-screw extruders and with mould temperatures of up to 300 °C to produce film, sheeting, and monofilaments. Extrusion products are often subdivided into groups that include filaments of circular cross-section, profiles of irregular cross-section, asymmetric tubes and pipes, and flat products such as films and sheets. The extrusion process is also used to cover continuous substrates with a polymeric layer (extrusion covering process) and is a major element of blow moulding and the film blowing processes. Mixtures of polymers, fillers, additives and so on (compounds) are often prepared in extruders.

Compression moulding is the process in which powder or granules of semi-finished product are put directly between tool faces, which are brought together under pressure to shape the material.

Machining quality is excellent for HDPE and fair for LDPE while mouldability is excellent for LDPE and good for HDPE. Ultrahigh molecular weight PE (UHMWPE) cannot be processed by standard shear methods because of its high viscosity (10^{10} Pa-s). Methods of processing this material are compression moulding, ram extrusion, and gel extrusion and spinning. Typical sintering pressures and temperatures for UHMWPE are 3–5 MPa and 180–220 °C, respectively. Because of the shrinkage rate of 4–6%, the rate of cooling is critical to the final dimensional stability of the moulded part. To prevent warping, the moulded form must be slowly cooled under pressure.

The economics of processing depend on the thermal characteristics of the material. The heat transfer requirement for cooling from the melt temperature to the mould temperature in the case of polypropylene (PP) is much higher than that for amorphous polymers. The thermal conductivity determines the cooling time of the material in the mould. Longer cooling times reduce the production rate. The thermal conductivity of HDPE at 20 °C is 0.43 W/(m K), the highest value compared with other plastics (0.16–0.23 W/(m K)). The heat transfer requirement for cooling from the melt temperature for HDPE is 750 kJ/kg, comparable with those of polyamide 6.6 (PA 6.6) (800 kJ/kg) and PP (640 kJ/kg). Semi-crystalline materials such as PE have higher specific heat capacities, and hence the energy required for melting is high and melt processing costly. The amount of heat removed from the mould during cooling is high and the cooling time is longer so cooling methods and design of cooling channels is important. The shrinkage between the melt and solid state is important. Therefore the dimensions of the moulding are difficult to predict and also warping, sinking, and voiding may occur. Higher die swell makes accurate extrusion profiles difficult. Blow moulding and thermoforming are more difficult in the case of amorphous polymers because of the low melt elasticity. The processing range is narrow.

6.1 Injection Moulding

The injection moulding process involves the rapid pressurised filling of a specific mould cavity with a fluid material, followed by solidification into a product. A high holding or packing pressure

(30–202 MPa) is normally exerted to compensate partially for the thermal contraction (shrinkage) of the material upon cooling. The pressure corresponding to a clamping force per unit projected area of cavity and feed system is in the range 0.3–0.9 tons/cm². Injection moulds must feature channels and cavities for fluid cooling and moving elements such as ejectors and retractable secondary sections. The parameters used in injection moulding depend on the PE grade (Table 6.1).

	LDPE	MDPE	HDPE
Temperature (°C)	572–1292	572–1292	572–1112
Pressure (MPa)	55–206	55–206	68–137
MDPE: <i>medium-density PE</i>			

The cooling of the material in the mould is the limiting factor in injection moulding, because of the low thermal conductivity of polymers. After the cooling stage the mould is opened and the solid ejected.

Injection moulding is a cyclic process. The period between starting the movement of the plunger or screw and the beginning of mould parting or opening is called the clamp time, because during this period the mould segments remain closed and clamped tightly. The injection cycle time is the clamp time plus the time required for the mould to be opened, the part to be ejected, and the mould to be closed again. Although the process of injection moulding is very simple, injection moulding machines and moulds are very costly due to the high pressure needed for injection and associated control. Fortunately, the speed of the process is high.

There are two types of injection moulding equipment: plunger-type (also called ram or piston) and screw-type machines. Linear low-density PE (LLDPE) requires more heat to be moulded than LDPE. These materials are more easily moulded in a screw machine in which the mechanical work of the screw adds considerably to the heat delivered by external electric heaters.

The projected area of a mould includes cavities and feed systems. The injection pressure is a function of part thickness, melt temperature, and mould temperature. It can vary within the mould. The three-zone reciprocating screw should achieve good plasticisation of the material. The estimation of the clamping force needed to keep the mould shut is a complex function of the projected area and the injection pressure. A rule of thumb for the clamping force required for PE is 0.2–0.5 tons/cm² of projected area. A large safety factor of 25–50% is advisable. Computer simulation of flow will provide a more accurate estimation of the injection pressure and mould opening force.

Similar to any semi-crystalline polymer, PE undergoes a greater volume increase than an amorphous material during melting. Hence the compression rate required for injection moulding of PE is lower.

The various machine and moulding parameters recommended for injection moulding of PE are given in Table 6.2.

The average injection pressure range is 600–1200 kgf/cm² for LDPE and HDPE, and 850 kgf/cm² for LLDPE. The holding pressure and time must be carefully controlled to avoid sinks and to compensate for high volume reduction when semi-crystalline material passes from the melt state to the solid state. Higher compression ratio screws (4:1) with a large length/diameter ratio of greater than 20 are required for filled grades and grades using masterbatches, to achieve good plasticisation and homogeneous melts. Usually, highly cooled moulds (15–30 °C) cause lower average linear shrinkage but can lead to warpage in parts with a high area-to-thickness ratio and are detrimental to surface gloss. Moulds that are too hot (80–90 °C) can lead to flashing, sink marks, and wavy surfaces. Moulding pressure and injection holding time have a major influence on shrinkage. For PE filled with long glass fibres, the decrease of shrinkage is only transverse, longitudinal shrinkage

Material	Melt temperature (°C)		Mould temperature (°C)		Drying time (h)	Drying temperature (°C)
	Low	High	Low	High		
HDPE	200	280	37	79	2	92
LLDPE	230	290–315				
LDPE	200	280	37	79	2	92
LDPE, MFR* 20 g/10 min	160	200				
LDPE, MFR 6.5 g/10 min	180	220				
LDPE, MFR 2.5 g/10 min	200	240				
LDPE, MFR 1.5 g/10 min	220	260				

* Conditions: 190 °C/2.16 kg
 LDPE: low-density PE
 MFR: melt flow rate

HDPE: high-density PE
 LLDPE: linear low-density PE

being almost independent because the filler induces polymer orientation. HDPE filled with glass fibres needs a hold pressure that is 50% of the moulding pressure. The cycle time depends on the wall thickness and mass of the part, increasing with both from 30 seconds for <3 mm thickness to 60 seconds for >5 mm thickness.

Additional rigidity, which is desirable for some parts, can be achieved in an economical manner by including ribs in the moulding. However, any sudden change in wall thickness due to the ribs gives rise to sink marks on the opposite side of the ribs.

Mould dimensions must be increased to take account of the average shrinkage of 1.5–2% for HDPE and 2–3% for LDPE, according to the thickness of the item (Figure 6.1). For filled PE, account must be taken of the reduction in shrinkage of 1.7 to 1.1% when the filler content increases from 15 to 45% independent of the filler type.

Degradation is associated with injection moulding of unfilled and filled PE, which can occur in two distinct ways: through overheating of the melt within the injection cylinder, cylinder head, and

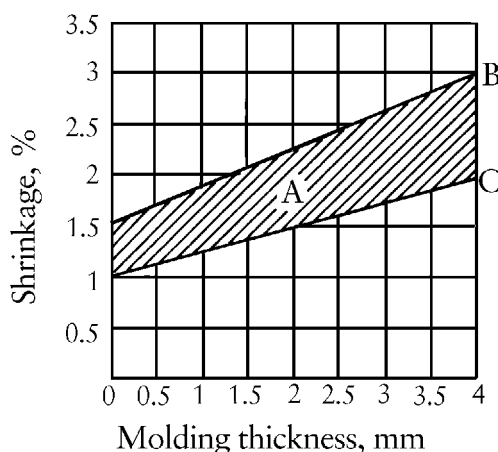


Figure 6.1 Shrinkage *versus* mould thickness [1]. Shaded area (ABC) indicates the most common variation in the two values

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nozzle; and through overheating by frictional shear created by the speed of the melt flow from the nozzle into the mould cavity. A temperature–dwell time diagram (Figure 6.2) shows the area of the incipient degradation. The selection of injection temperature must be made according to this diagram, although to fill the mould the highest temperature is optimum.

The shot volume for an injection moulding machine is a function of the screw diameter and its maximum retraction during plasticising. Quoted injection weights are usually referred to polystyrene (PS). The melt densities of PS and PE are 0.89 and 0.745 g/cm³, respectively. This means the shot weight for PE for a particular injection machine will be less than that for PS on the same machine. The shot weight for LDPE and HDPE for a particular injection-moulding machine is lower than for other plastics, particularly PP. Shot volume is limited by the residence time. The allowable residence time depends on the material temperature and the nature of heat stabilisation. Longer residence times are possible at lower temperatures. The shot volume may be up to 85% of the maximum shot volume of the machine. The minimum shot volume depends on the residence time and can be as low as 15% of maximum shot volume of the machine.

PE normally requires no pre-drying before injection moulding, with some exceptions, such as when stored under unfavourable conditions or when filled grades are processed. In the case of filled grades or dark-coloured material, additional enhancement of the surface quality can be achieved by pre-drying at 120 °C for three hours in a dried air circulating oven.

Moulding conditions are quite unique to the article being moulded and depend on the part configuration, mould design, material properties, choice of material, and properties required for the finished part. PE can be injection moulded at a melt temperature of 200–240 °C and a mould temperature of 20–90 °C. Lower mould temperatures may be used for fast cycling of parts at a high injection rate. High mould temperatures are required for thick-walled parts where premature solidification of the walls may lead to the formation of internal voids. Higher temperatures can result in discoloration and thermal degradation and can also lead to the corrosion of the mould and the machine. The melt temperature of the easy flowing grades should be kept low, as the material manufacturer recommends. For small parts, many moulds are often mounted on one machine and the molten plastic is injected into them all simultaneously. Injection moulding can produce far more complex items than extrusion, but it is not a continuous process.

UHMWPE and HDPE processed by shear-controlled orientation in injection moulding (SCORIM) exhibit a reduction in the formation of microvoids and microcracks and an enhancement in wear resistance.

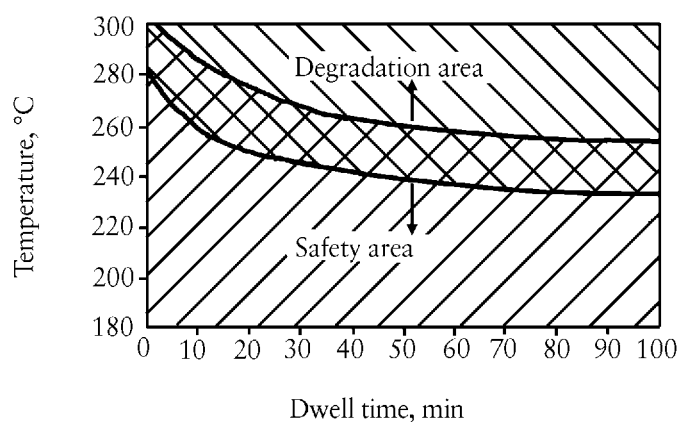


Figure 6.2 Area of incipient degradation (cross-hatched area) of a polyolefin related to the temperature and dwell time of the injection cylinder [1]

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Injection moulded articles represent only a small proportion (5%) of the consumption of LDPE and LLDPE. This proportion is not insignificant, however, considering the total volume of 300,000 tonnes per year. LDPE and LLDPE parts produced by injection moulding are used in a wide range of applications, for example, for domestic storage containers and closures in cosmetic, food, and pharmaceutical applications. High environmental stress crack resistance and low warpage are required for LLDPE applications.

6.2 Extrusion

For the extrusion process, plastic in the form of pellets or powder (dry blends) is fed into a heated cylinder where rotating screws homogenise it and squeeze it through a die to give a finished or semi-finished product. Pellets are used in single-screw extruders and powders are used in twin-screw extruders. The die is designed to produce the desired shape of the end product.

Extruding can produce soft or rigid items, which can be compact or cellular in form. For producing hollow articles, a special tool is required and this process is called extrusion blow moulding. Profiles that require an aesthetic appearance are made by the co-extrusion process which uses two extruders and a specially shaped die.

Many film extruders and film markets are reaping the benefits of properties offered by advanced Ziegler–Natta and high-strength linear PE. To achieve the full benefit from these polymers, it is necessary to determine optimum extrusion conditions, especially for LDPE, where the absence of long-chain branching (LCB) causes polymer chains to orient in the machine direction. Branch length is controlled by the type of monomer used in the manufacture of the PE. Butene monomer PE have two carbon length branches, hexane comonomer PE have four carbon length branches, and octane comonomer PE have six carbon length branches. Linear PE also have a relatively narrow MWD and have higher viscosity at a given shear rate in comparison to traditional LDPE. These differences result in higher extrusion power, back pressure, and melt temperatures during extrusion.

Film extruders who routinely process LDPE must often make modifications to equipment, or, at the very least, the temperature profile, to produce films with good physical properties. Melt fracture, or sharkskin, can be a problem at high die shear rates. This can be eliminated by raising extrusion and die temperatures, by increasing the opening of the die to reduce shear, or by using polymer processing aids. The key extrusion parameters that affect final film properties are blow-up ratio (the ratio of the bubble diameter to the die diameter), die gap, output rate and so forth.

6.2.1 Film Extrusion

PE film extrusion represents one of the largest individual plastics processing sectors and accounts for over 6.5 millions tonnes representing more than 20% of the total polymer market. The major part of the demand is accounted for by the use of conventional LDPE (~55%), but the use of other grades of PE, especially linear and metallocene resins, has increased to around 28%. Shrink and stretch film has emerged as the strongest performing market sector and technical co-extrusions reflect the increasing demand for linear grades and HDPE resins, although metallocene resins have also made an impact on these markets. The largest end-use application for PE film is for bags and sacks, which account for around 40%, and shrink and stretch packaging, which account for around 25% of the PE film market.

The greatest number of PE film extrusion plants in Europe is located in Italy whereas the larger companies tend to be located in Germany and Belgium. The number of independent film extrusion sites has declined as the producers have been bought up by larger groups such as British Polythene Industries (UK), Trioplast and Amando Alvarez (Western Europe), and TVK (Central Europe).

The suitable extrusion conditions for PE are given in **Table 6.3**. The compression ratio ranges from 3:1 to 4:1. A length-to-diameter ratio of >20 can also be used for filled PE. The barrel can also

Table 6.3 Extrusion parameters for PE in various products

PE type	Temperature (°C)						Pressure (MPa)	Extrusion temperature (°C)	Length/diameter ratio
	Barrel zone				Forming device	Die			
	1	2	3	4					
LDPE pipes	125	125	130	130	130	125	7.5–15	160–190	18
LDPE cable coating	160	210	230	240	230	235			
HDPE pipes	140	160	165	165	165	170	10–17	170–230	20–24
HDPE sheets	220	190	170	165	165	170	10–17		
HDPE cable coating	200	210	240	250	240	245	25–30		

improve the material conveying performance at the inlet, stepping up the output rate. Normally PE is not likely to contain moisture, volatiles, or entrained air, so vented screws are normally used in its processing.

In recent years LDPE has been increasingly replaced by all types of LLDPE, due to the latter's better mechanical properties compared to LDPE, and the resulting properties for reducing the film thickness. The problem of the poor processing properties of LLDPE has been resolved by the progressive improvement of film blowing machine technology.

Metallocene-catalysed PE (mPE) grades are firmly established in almost all PE film applications. This class of raw materials plays an important role in the production of stretch films, heavy-duty bags, and laminating films. For heavy-duty film bags, processors have succeeded in reducing the minimum film thickness from 180 to 120 μm by employing mPE in the last few years. Apart from the improvement in raw material, the trend towards three layer co-extrusion has certainly contributed to this application.

Stretch film of all types of LLDPE can be produced very economically on cast film lines with throughput rates of up to 2 tonnes/hour. The state-of-the-art is five layer technology.

In recent years breathable PE film for personal hygiene applications has been developed. Traditional 'backsheet nappy film' of LDPE is increasingly replaced by LLDPE film grade. This breathable film is usually manufactured from chalk compounds based on LLDPE or metallocene LLDPE. After extrusion, the films are subjected to stretching in order to introduce microperforations into the film at the interface between the polymer and the chalk particles.

Stretch hoods for securing goods on pallets can be produced as an alternative to shrink hoods with much lower raw material consumption. Stretch hoods do not need to be heated with hot air or an open flame. The predominant raw materials are ethylene-butyl acrylate (EBA) and ethylene-vinyl acetate (EVA) copolymers.

Extrusion coating of LDPE is used for coating paper, cardboard, and aluminium for milk and fruit juice packaging.

Shrink films are commonly used as an over-wrap for sensitive goods, since they confer protection, make transportation easier, and contribute to the aesthetics of the product. LDPE is known to be the most suitable product for producing these shrink films. Because of the presence of long-chain branches, stress tends to develop in the melt during the film fabrication process, and the frozen stressed structure relaxes when exposed to temperature leading to film shrinkage. LDPE shows good shrinkage in both the machine and transverse directions so can be used for light packages. Conventional LLDPE is not indicated for such an application due to the lack of shrinkage in the transverse direction. When heated it expands instead. However, the use of LLDPE would lead to improvements in tensile strength and puncture and tear resistance compared with LDPE, and make downgauging easier.

The MWD has an important effect on the output rate, extruder torque, and pressure development in the extruder. Polyolefins with a narrow MWD have a higher output rate, extruder torque, and pressure development during extrusion than those with broad MWD. The die length has no significant effect on film structure and on factors such as tensile, tear, and impact properties.

6.2.2 Co-extrusion

Co-extrusion has gained importance for the production of blown and cast films. Co-extrusion allows the property profiles of various PE to be combined. The film properties can therefore be adapted to the particular demands with extremely economical material consumption. Tried and tested designs of multilayer extrusion dies permit the formation of extremely thin layers, even under difficult rheological conditions.

Co-extruded films have a very complex structure, being composed of many layers providing different functionalities and of different tie layers that improve the bonding between adjacent layers. Separate extruders are required for extrusion of the different layers. Viscosity of resins and adherence between layers are very important.

Agricultural films are used to increase crop yields, extend the climatic range under which crops can grow, conserve water and energy, reduce pest infestation, and store animal silage. Films can be tailored for given geographic regions and specific uses. Fluorescent films utilise colorants able to absorb light. The fourth generation of film for agriculture will be co-extruded blue film with a light-blue colour in contact with the ground and a yellow layer on the outside. This should allow the transmission of green light for photosynthesis, while the yellow colour repels insects. New developments are photoselective mulching film of red colour to cover tomatoes and roses or a pink colour for peppers. 'Plasticulture' uses films that resist UV photodegradation. Thermic films retain the heat emitted from the earth's surface during the night and can be used in greenhouses to retain this heat. Photoselectivity is another important property. Three layer films make it possible to combine appropriate basic polymer properties and additives in each layer. A typical three layer film is LDPE/EVA/LDPE. LLDPE is used for mulching because of its good mechanical properties that allow low-thickness film to be produced.

6.2.3 Sheet Extrusion

Sheets are thicker than films, being thicker than 0.25 mm. They can be produced with slit dies in a range of widths and thicknesses. The width of the sheets may be as much as 2.5 m. Sheets may be used for further fabrication such as thermoforming, machining, welding, and laminating. They are produced from low-MFR material. The key advantages of PE sheets are good rigidity-to-thickness ratio, toughness, moisture resistance, and chemical resistance, non-toxicity, and good moisture barrier properties.

6.2.4 Extrusion of Compact and Expanded (Foamed) Polyethylene

Extrusion of compact and expanded (foamed) PE takes place on the same type of extruder using the operational parameters given in **Table 6.4**. The recommended screw profile for the feed zone is $2D$, for the compression zone is $13D$, and for the homogenisation zone is $5D$; $L/D > 18$ (L is the length and D the diameter). The compression ratio is 2.5–3. A laminar flow through the die is essential for good-quality foam. The expansion degree is inversely proportional to rotation speed and residence time.

6.2.5 Ram or Cold Extrusion

Tube, rod, and profiles are extruded at low temperatures and require an extruder producing a minimum of heat build-up, approaching the ideal of adiabatic performance where all, or nearly all,

Polymer	Temperature along the extruder (°C)					Rotation speed (rpm)	Density (g/cm ³)	Concentration of the blowing agent (%)
	Die	Head	Zone 3	Zone 2	Zone 1			
HDPE	195	200	200	175	165	–	0.5	0.5
LDPE	190	220	220	225	130	–	0.33	0.7
EVA	150	160	170	170	135	–	0.33	0.75
HDPE + LDPE, 9:1	210	230	190	165	140	60	0.68	0.45

but not more than the required heat is generated by mechanical work. Extrusion is generally started at about 150 °C. The temperature is then reduced with careful attention to the pressure, either until a satisfactory rod is produced or until the pressure exceeds a safe pressure for the machine. Pressures of 41–55 MPa are frequently required.

The process employs a reciprocating ram to compact and transfer UHMWPE powder through a heated die. When the ram is reversed, fresh powder flows into the vacated cavity and the process is repeated. The compacted and fused powder moves through the die as a succession of charges are formed into a continuous profile. The process is quite different from the more common melt extrusion processes. No shear mixing of polymer takes place in ram extrusion. Unlike melt extruders, backpressure in ram extruders is not developed by constriction of the die channel. The axial die pressures during compaction are high, approximately 44 MPa. The processing conditions of pressure, temperature, extrusion rate, and die geometry are interrelated.

UHMWPE powder compaction and sintering by either extrusion or compression moulding yields similar values in terms of the final mechanical properties of the polymer. The resultant moulded semi-forms can be easily shaped (cut, turned, sawed, milled, or punched) using standard machine tools. UHMWPE is difficult to bond using adhesives but parts can be joined effectively by butt welding or mechanical fasteners.

Die drawing allows bars, tubing, and large-size sheets to be obtained. The polymer is drawn through a heated die with a conically shaped entrance. Sheets of oriented polymer can be produced by roller drawing while highly oriented films and rods can be obtained by co-extrusion.

It is convenient for the extrusion of LLDPE to blend it with about 10% LDPE to increase flow, reduce weld lines, and improve the general quality and homogeneity of products.

The support and control of the extrudate after leaving the die is the main problem in the production of pipe. In the ring method, air pressure is maintained inside the tube, which is passed through a succession of ring orifices. In the internal mandrel method, a water-cooled extension is attached to the end of the die mandrel. In the vacuum-sizing chamber method, the pipe enters a tube with a perforated section in the centre, through which a slight vacuum is applied to hold the pipe against the walls of the sizing chamber. Reheating of the pipe at about 115–120 °C in a liquid bath (glycerol) and stretching it by internal pressure to the inside of a die with a larger diameter permits the manufacture of biaxially oriented pipe with a greater strength and stiffness, improved resistance to creep, and long-term burst strength.

6.2.6 Extrusion of Wire and Cable Covering

These coatings range from 0.25 mm or less for fine communication wire to coatings 6 mm thick on cable sheathing. The extruder and extruder conditions for these applications vary from conditions similar to those for pipe extrusion for heavy sheathing to conditions similar to those for monofilament

extrusion for fine wires. Foamed insulation can be applied to wire using a PE containing a compound capable of releasing gas at the extrusion temperature.

6.2.7 Extrusion of Monofilament

Monofilament is usually extruded using a conventional screw extruder of rather small size, through a die consisting of a series of holes. The monofilaments are extruded downward into a tank of water (quench tank) from which they go to pull-rolls to be drawn and oriented. The physical properties of the strands depend on the conditions of extrusion, on the degree of stretching, and on the temperature at which they are stretched. For HDPE, a melt temperature of between 260 and 290 °C is usually best. For LDPE, about 30 °C lower is better. Strength increases with draw ratio and generally levels out at ratios between 9:1 and 12:1.

6.2.8 Cast or Blown Film [2]

Blow and cast film extrusion are the common methods in film production. Blow film extrusion is a major method for producing bags from LDPE, LLDPE, and HDPE.

Film blowing consists of extruding a tube of molten thermoplastic and continuously inflating it to several times its initial diameter, to form a thin tubular product that can be used directly, or slit to form a flat film. The molten tube gradually deforms into a stable solid cylindrical bubble beyond the frost (freeze) line. The bubble is then flattened in a collapsing device (tent frame), which consists of a pair of converging ladder-like sets of idler rolls or wood slats, and beyond pinch (nip) rolls it is handled as a thin flat product. The blow-up ratio (BUR), defined as the ratio of the bubble to die diameter (or circumference), is normally in the range 1.5–4, such values requiring high melt strengths. The air pressure in the bubble, which is responsible for the blowing, is normally in the range 5065–20265 Pa. Machine direction drawdown is associated with the take-off velocity.

Cast films have been able to win a significant market share in the area of thinner or fine films, particularly for flexible packaging applications, in the last 25 years. These films are extruded from thermoplastic polymers through a slot die onto a water-cooled chill roll giving a rapid quench type cooling of plastic melt, producing a film with an excellent optical thickness gauge profile, owing to the use of a slot die with a flex lip design, actuated either manually or by automatic profile control. The film thickness is controlled by the gap between the die lips but also by the rotational speed of the chill roll. The rapid quenching of the film by direct water cooling reduces the crystallinity and produces a tough film.

Their excellent optical properties, notably gloss and haze, gauge tolerance, and the lower capital investment of a cast film extrusion line (less than half that of a biaxially oriented PP (BOPP) line) have enabled cast film to maintain its market presence, despite the superior mechanical properties of oriented blown film. The disadvantages of cast films are their tendency to split and very low transverse strength.

More recently there has been extensive growth in cast stretch films, based on LLDPE resins, particularly in the area of pallet stretch wrap, for which pre-stretching of up to 300% and even higher is required.

Today, virtually all cast film extrusion systems sold are for co-extrusion, generally for three to five layer films, although cast films of seven layers for higher barrier applications are available and lines for up to 11 layers exist at least in the design form. An example is the development of the so-called 'high-end' stretch film market based on five layer structures with the incorporation of layers from mPE. Extrusion line speeds of 400–500 m/min for PE-based stretch films are considered state-of-the-art. The processing conditions include: (a) design of extruders not only with traditional shear and mixing screws, but also barrier screws to deliver a homogeneous melt at higher outputs at the

higher torque requirement of LLDPE and metallocenes; (b) edge trim proportion of up to 200 kg/h and higher; (c) precise slit die and co-extrusion adapter technology that enables ultrathin layers of 2 μm or less; (d) high stabilisation of film web in the cast roll unit to enable the highest possible speeds by means of sophisticated air knife and vacuum box technology and super-high-quality casting roll surfaces; and (e) the maximum possible automation and lowest possible cycle time of finished roll removal and handling processes. **Figures 6.3–6.5** show the dependence of output rate, Q , and energy consumption, A , on screw rotational speed for four PE, namely LDPE, HDPE, and two mPE having the same MFR [3].

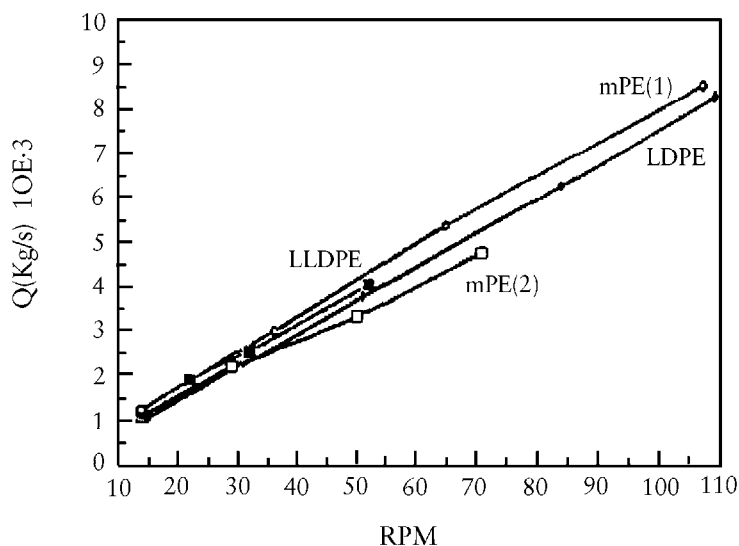


Figure 6.3 Dependence of output rate on screw rotational speed for mPE(2) (\square), LLDPE (\blacksquare), mPE(1) (\diamond), and LDPE (\blacklozenge) [3]

Redrawn from C.M. Wong, H.H. Shih, C.J. Huang and A.M. Sukhadia in *Metallocene-Catalyzed Polymers – Materials, Properties, Processing and Markets*, William Andrew Publishing/Plastics Design Library, 1998. Copyright William Andrew Publishers, 1998.

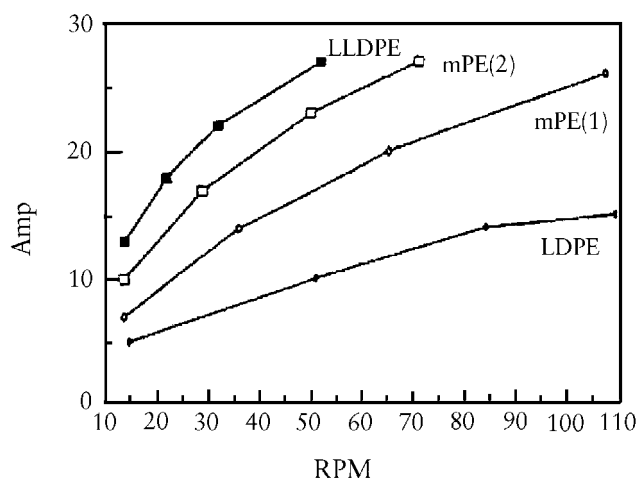


Figure 6.4 Dependence of energy consumption on screw rotational speed for mPE(2) (\square), LLDPE (\blacksquare), mPE(1) (\diamond), and LDPE (\blacklozenge) [3]

Redrawn from C.M. Wong, H.H. Shih, C.J. Huang and A.M. Sukhadia in *Metallocene-Catalyzed Polymers – Materials, Properties, Processing and Markets*, William Andrew Publishing/Plastics Design Library, 1998. Copyright William Andrew Publishers, 1998.

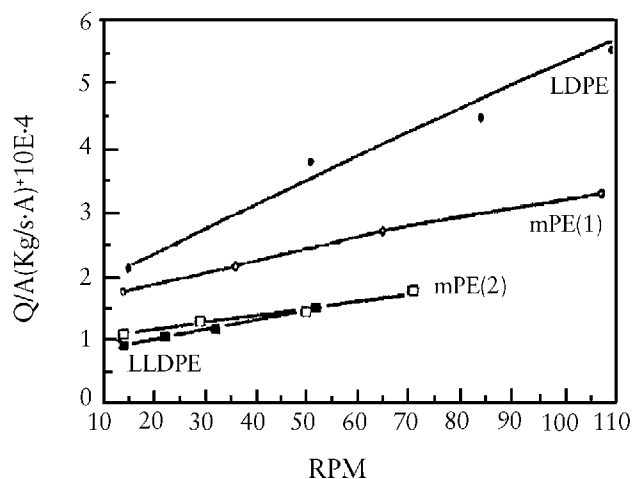


Figure 6.5 Dependence of output rate per unit energy consumption on screw rotational speed for mPE(2) (□), LLDPE (■), mPE(1) (◇), and LDPE (◆) [3]

Redrawn from C.M. Wong, H.H. Shih, C.J. Huang and A.M. Sukhadia in Metalocene-Catalyzed Polymers – Materials, Properties, Processing and Markets, William Andrew Publishing/Plastics Design Library, 1998. Copyright William Andrew Publishers, 1998.

There is a relationship between bubble stability and processing conditions and material properties. A material containing LCB normally has a high melt strength. A high melt strength can result in good bubble stability in film blowing. At equal MFR level, the melt strength of LDPE is about twice that of LLDPE and HDPE. An increase of processing temperature can lead to a decrease of bubble stability. BUR and drawdown ratio (DDR) (take-up speed by nip rolls to line speed of polymer melt through the die lip) are important factors affecting bubble stability. Different thicknesses of blow film are produced by different DDR and BUR. Bubble stability is a key factor to make a uniform film.

The four materials of **Figure 6.3** have similar output rates at low screw speed. When the screw speed increases, PE with narrow MWD has higher output rate than broad MWD material. The order of energy consumption at a particular screw speed is LLDPE > mPE > LDPE (**Figure 6.4**). **Figure 6.5** shows the experimental results of output rate per unit energy consumption at various screw speeds. LDPE appears to have the highest value, indicating that it needs less energy during extrusion than the other types of PE. LLDPE and mPE (hexene monomer) are extruded at a screw speed of less than 70 rpm due to the limit of energy consumption, but LDPE and mPE (octene monomer) can be extruded at a screw speed of more than 100 rpm. Therefore LCB strikingly affects the flow behaviour of material in extrusion.

Comparing the bubble conditions (stable, unstable, and metastable) in film blowing at various DDR and BUR with a certain frost-line height (**Figure 6.6**), it appears that LDPE has a wide region of bubble stability, but LLDPE does not. Generally LLDPE is more difficult to process in film blowing than LDPE. A possible way to obtain stable bubbles for LLDPE is to control the frost-line heights below a certain value. The order of the ranges of frost-line height at which stable bubbles are found is LDPE > LLDPE > mPE (octene) > mPE (hexene) (**Table 6.5**). These ranges are used to evaluate the processability of materials in film blowing. Metalocene PE are generally more difficult to process in film extrusion than LDPE and LLDPE.

LCB in PE can be introduced by peroxide addition, radiation treatment, finishing/stabilisation, and appropriate polymerisation conditions.

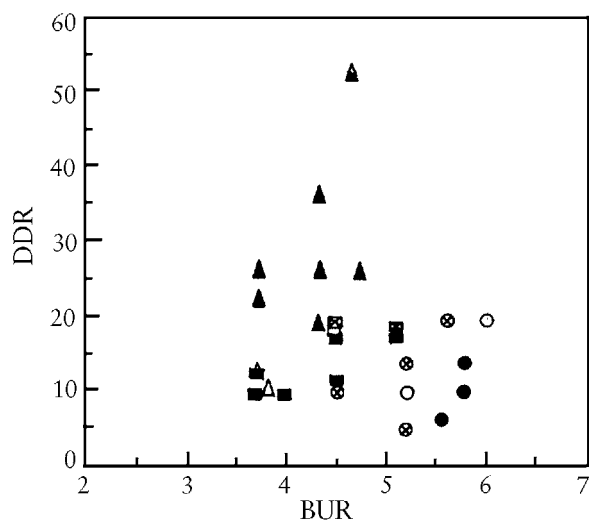


Figure 6.6 Bubble conditions at various drawdown ratios (DDR) and blow-up ratios (BUR) with frost-line height of 0.2 m for LDPE (■: stable; □: metastable; ×: unstable), LLDPE (▲: stable; △: metastable, ×: unstable), and mPE(1) (●: stable; □: metastable; ×: unstable)

Redrawn from C.M. Wong, H.H. Shih, C.J. Huang and A.M. Sukhadia in Metallocene-Catalyzed Polymers – Materials, Properties, Processing and Markets, William Andrew Publishing/Plastics Design Library, 1998. Copyright William Andrew Publishers, 1998.

PE type	Range of frost-line height having bubble stability, min–max (m)	Difference (m)
LDPE	0.1–0.35	0.25
LLDPE	0.1–0.25	0.15
mPE (octene)	0.15–0.25	0.10
mPE (hexene)	0.07–0.14	0.07

Reifenhauser India offers 250 cast film systems classified into three types: compact lines with 1900 mm chill roll width; MIDEX medium-capacity lines up to 3000 mm; and HIPEX high-output lines wider than 3000 mm with output >1200 kg/h.

Applications include multilayer barrier films with PA6 (polyamide 6)/ethylene–vinyl alcohol (EVOH)/PA6 for the highest barrier applications especially for medical products, co-extruded cast films based on PP or PE with fillers such as calcium carbonate monoaxially stretched to achieve breathability to provide a water barrier but enabling water vapour to permeate the film, used in domestic wrapping, roof underlay applications, hygiene products, for example, nappies and feminine care.

Five layer cast adhesive stretch films are obtained from LDPE. In the blow film process, internal air pressure is used to produce a relatively thin film. Normally air is used as a coolant for PE film.

6.2.8.1 Biaxially Oriented Film

This type of film can be produced using a blow film or a tenter process. Stretching in both the machine direction and transverse direction is carried out at a temperature below the melting point of the polymer and results in the partial orientation of molecules in the direction of stretch. The

film produced by the blow process is nearly isotropic in both directions while the film produced by the tenter process tends to be more highly oriented in the direction of the machine. The cost of the tenter process equipment is much higher in comparison to blow film equipment. Biaxially oriented films are not easily heat sealable.

6.2.9 Stretched Tapes

Strapping tapes, film tapes, monofilaments, fibres, and non-wovens are usually stretched immediately after extrusion to achieve considerable increase in ultimate tensile strength in the stretching direction as a result of molecular orientation. The elongation at break correspondingly decreases. The film for stretched tapes can be produced by a cast film technique using either the water quench or chill roll process.

6.2.10 Pipes, Tube, and Conduits [4]

For plastic pipes, LDPE and LLDPE are used less than HDPE. Typical applications are irrigation lines or flexible tubes with small dimensions.

PE is the material of choice for pipeline applications. These include both pressure and non-pressure applications for gas and water distribution systems. Pipe applications require the product to be installed in the ground for lifetimes sometimes in excess of 100 years. PE systems offer significant advantages over so-called 'traditional' iron, steel, and cement systems, in particular resistance to corrosion whatever the ground conditions. The flexibility of PE pipe allows it to be coiled and supplied in long lengths avoiding frequent joints and fittings giving substantial cost saving during installation. A PE system has an inherent resistance to the effect of ground movement from temperature fluctuation or instability. No protective layers or finishing processes are required, thus avoiding additional expense and further potential risk of failure due to damage prior to or during installation. High levels of strain can be safely tolerated since the associated initial stresses in the pipe wall relax and redistribute as the pipe system becomes increasingly stable while settlement and compaction take place.

PE is often colour coded to enable the application of the pipe to be identified. Typically, this is blue for water and yellow for gas, or coloured stripes on black pipe. The material is biologically inert and is not subject to rodent attack. Other advantages are that it is of low weight and resistant to site handling, it can be produced as leak-free fusion jointing systems (which do not allow root penetration), it has improved hydraulic capacity from low-friction bore, it is not subject to scale build-up, its flexibility allows a range of cost-effective installation techniques to be used, it has a track record of reliability and durability in service, and it has a cost-effective long maintenance-free lifetime/low whole-life costs. As a liner or coating it provides corrosion protection to allow the use of a cheaper-grade steel host pipe. Liners can be inserted on site or *in situ* for renewal purposes.

A PE system is normally limited to pressures of 1 MPa for gas and 1.6 MPa for water applications to avoid excessively thick products. The upper service temperature limit is normally around 40–50 °C but this is extended by the use of crosslinked PE (XPE) to around 80 °C or more for liner applications. The development of reinforced and multilayer pipe systems continues to extend such limits. The size range for water is 16–1600 mm, while for gas it is normally up to 630 mm.

For drainage and irrigation applications, flexibility and good stress crack resistance have enabled PE to be used in many forms. Telecommunication systems using fibre optic transmitters, cable TV, power signal, and lighting have successfully used PE ducting to prevent damage to cables in service.

XPE is used for water supply lines (cold and hot potable water distribution being consistent with the requirements of the Environmental Quality Act) and irrigation pipelines. It has been used since about 1985 in the USA and earlier in Europe. There are many reasons why PE pipes are popular.

They are 100% leakproof, durable, flexible, economical, and tough, they do not corrode, are easily welded into large lengths, and provide resistance to a wide range of chemicals. Because of these characteristics it was appreciated that the resulting pipe system has a minimum lifespan of 100 years. Competing materials for such applications are polyvinyl chloride (PVC), iron, and others. The increase in the use of PE pipes compared to other materials is shown in **Figure 6.7** [5].

Aluminium/plastic composite pipes for heating and sanitary applications are manufactured in five layers: two layers of silane-crosslinked HDPE with an aluminium core and two adhesive layers. The aluminium layer provides an oxygen barrier.

HDPE pipes reinforced with aramide tape can withstand 7.0 MPa operating pressures for service lives of 50 years. Multilayer pipes are made of a standard PE inner layer wrapped with aramide tape.

Metal pipe ruptures when freezing water expands. Flexible plastic pipe does not. Depending on local codes, it need only be buried deep enough below the surface to protect the pipe against accidental damage from digging or cultivation. XPE is cheaper to buy and install than copper pipe.

PE has excellent chemical and crush resistance as well as high impact strength and flexibility. It functions at temperatures from -54 to $+50$ °C in low-pressure applications and to 93 °C in non-pressure applications.

Couplings are not required in PE pipe unless the pipe is cut. PE pipe is joined using polyamide or brass fittings and stainless steel clamps and clamp screws.

PE is used in low-pressure water systems, such as golf course sprinklers, for corrosive liquids and gases, in underground conduits, and as gas pipe re-liner. It is also used in industrial and chemical laboratory drainage systems, and for underground gas piping.

The strength of flexible or semi-rigid PE pipe decreases as the temperature rises. Therefore in high-pressure lines it is used for cold water only. It has pressure ratings between 0.55 and 1.10 MPa. It can be cut with a pocket-knife. Any plastic pipe used to carry drinking water should have the seal of the National Sanitation Foundation.

PE pipe is used for hot water heating in concrete floors. Temperatures of up to 38 °C are common for foot comfort. For this use, however, the best brand of virgin plastic rated at 46 °C should be used. Also, mixing valves for water temperature control should be installed.

Lines should be laid in straight lines to avoid undue stress. PE pipe is available in diameters of up to 150 mm or larger, and it can be joined using threads and clamps.

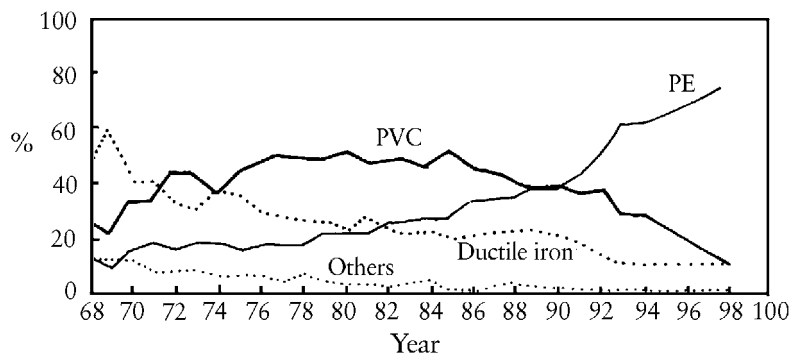


Figure 6.7 Comparison of materials used for pipe manufacture (1968–1998) [5]
Redrawn from R. Asman, Plastics News International, March, 6, 2003. Copyright 2003.

Pipes and fittings should have high impact strength, a homogeneously fine structure throughout the thickness of the pipe, and low frozen-in stresses. Thick-walled pipes made of conventional PE tend to have a coarse morphology in the middle of the wall. Frozen-in stresses are undesirable because pipes are subjected to internal pressure stresses in operation. Early failure may result where these are combined with external stresses. PE 100 materials, which are characterised by their combination of high stiffness and toughness, have extended PE applications to higher operating pressures. For gas lines, 1 MPa is now standard, and 2.5 MPa lines are used for drinking water. One development has been the reduction of sagging for large pipe diameters and high wall thicknesses. Improved PE 100 grades, such as multimodal Hostalen pipe grades, now allow the production of large, thick-walled pipes with a uniform wall-thickness distribution.

New pipe concepts with multilayer structures, or so-called functional layers, have helped to expand the applications of HDPE. Pipes with special protective layers (on the outside and/or inside) can be laid without a sand bed under some circumstances. This significantly reduces the pipe laying costs. There have also been new developments in joining technology. For example, electric welding fittings up to 700 mm are now available. Electrofusion jointing of PE pipes for gas distribution is also applied.

For steel pipe coating, newly developed bimodal HDPE grade, combined with new grafted adhesion promoters, has extended the applications window for PE as a corrosion protection layer towards higher service temperatures. This new bimodal HDPE sheathing material is increasingly replacing the MDPE and LDPE grades used until now in modern three layer systems (consisting of epoxy resin, LDPE/LLDPE adhesion promoter, and PE cover layer).

Perforated PE is used as corrugated drainage pipe. Corrugated pipe is soft, flexible PE pipe sold in lengths or in coils and used for drainage around building foundations and for other ground drainage situations. It may either be solid or perforated to permit seepage. Multilayer pipe is used for underground potable water transportation. Future development aims of the HDPE pipe market include new HDPE grades with further improved stiffness/toughness properties (PE 125).

6.3 Blow and Stretch Blow Moulding

The basic principle of the blow moulding process is to inflate a softened thermoplastic hollow preform against the cooled surface of a closed mould, where the material solidifies into a hollow product. The process is called 'extrusion injection moulding' when the preform is produced by extrusion, or 'injection blow moulding' if it is injection moulded. In conventional extrusion blow moulding, and to a large extent in injection blow moulding, the material deformation is primarily circumferential, leading to an unbalanced orientation in products. A technique referred as stretch blow moulding gives injection-moulded preforms a more favourable biaxial orientation. Blowing pressures are often limited to normal plant air pressure (about 0.83 MPa), and clamping forces are thus relatively small (typically about 1 tonne for a bottle and about 150 tonnes for a shipping drum). For very large products, self-locking moulds have been used.

For larger containers, the molten resins have to be extruded very quickly or 'sagging' will occur due to gravity. This is called intermittent extrusion, which usually only produces one or two containers for each machine cycle. For smaller containers like those for dairy products and fruit juices, there are machines that can produce up to 16 containers at a time. This allows them to process a high quantity of containers to meet the demands of industry.

As a blow moulding material, use of HDPE has been very successful. In order to work at the lowest practical temperatures, very good temperature control is necessary for all stages of the process, and in addition machines should be of robust construction because high pressures are developed in the barrels. To minimise wear the extruder barrels should have a continuous hardened steel liner.

The material most generally used is HDPE, and grades with MFR values as low as 0.1 or even 0.01 can be blow moulded quite readily. For LDPE a MFR range from 0.5 to 0.8 is suitable. A typical melt temperature is 191 °C.

Some recommended conditions for the processing of blown films are listed in **Table 6.6**.

Melt temperature (°C)	180–200
Blow-up ratio	1.5–3.5 or 3–5

The critical requirements for the screw design are to achieve high production rates with good plasticisation of the material without degradation. Conventional extruders with screw lengths greater than or equal to 20 and smooth barrels, or with barrels with a grooved feed zone can be used for plasticisation. The latter offer the advantage of output rate and uniformity. Conventional blow moulding imparts a degree of circumferential orientation caused by the expansion of the parison in the mould cavity, but there is no preferential axial expansion or orientation. Stretch blow moulding processes are designed to produce biaxial orientation in the blow articles.

LDPE is generally used for small volume blow moulded articles, mainly for household, domestic, and pharmaceutical applications. Due to its high purity, LDPE is the preferred raw material for medical and pharmaceutical packaging applications. In the pharmaceutical field, blow moulded articles have a particular importance because they can be filled under sterile conditions immediately after production, while still in the blow moulding machine (blow–fill–seal process). To ensure sterilisation, higher density LDPE is preferred.

A three layer coating comprising epoxy resin, LDPE copolymer as adhesion promoter, and LDPE cover coat is an efficient and durable corrosion protection for steel pipes that can be effective for over 25 years. Nowadays, the trend is towards grafted LLDPE as an adhesion promoter with higher heat resistance and better adhesion promotion in combination with MDPE and HDPE products as sheeting material.

6.4 Fibre and Filament

Among the methods for converting polyolefins into fibres and filaments are dry and wet spinning and melt spinning. The modern methods are high- and ultrahigh-speed spinning, the split-film method, the spunbond process, and the melt-blow system. Solution gel-spinning technology is applied for UHMWPE. Because of the high rate of crystallisation of PE and PP, the effect of molecular orientation can be controlled only by high speed melt spinning from these polymers. In gel extrusion and spinning, UHMWPE particles absorb oil, swell, and form gels that can be extruded on modified plastic screw extruders and fibre lines. Subsequent extraction of the oil from the formed sheets results in a porous material suitable for battery electrode plate separators or filter membranes. The majority of automotive lead-acid batteries manufactured today contain UHMWPE electrode plate separators produced in this manner.

Orientation prior to extraction of oil from gel filaments can also produce fibres called gel-spun fibres with the highest specific tensile properties of any polymer fibre (tensile modulus of 220 GPa and maximum tensile strength of 6.0 GPa). A modern wet-spinning technology known as solution gel spinning is now used for UHMWPE ($M_w = 500,000\text{--}5,000,000$) to obtain extended-chain PE fibres. A dilute solution, in which macromolecules can disentangle, is prepared and then spun. During the quenching process, a gel fibre develops in the filaments. The solvent serves to disentangle the polymer chain during spinning and drawing, with the formation of an extended-chain configuration.

This special structure imparts strength and stiffness to a yarn. For orientation in the fibre direction and subsequent crystallisation one or multiple drawing processes follow. The yarn may be treated with suitable finishes and dye acceptors before spooling. Of special interest are PP and PE filament yarns with high strength and high modulus of elasticity, formed by using high draw ratios (~1:30) at elevated temperatures or in non-isothermal multistage drawing processes. This is achieved by high orientation without chain folding, PE being basically better suited for this process than PP.

Spinning conditions for PE are an extrusion temperature of 290 °C, take-up speed of 200–3000 m/min, and a quenching temperature of 278 °C.

Among non-conventional technologies, film tape and film fibre processing are the most important. Film-to-tape and film-to-fibre processing are economically justifiable when the film process is simple and inexpensive. Only polymers with weak intermolecular forces (HDPE and PP) producing film at high stretch ratios and pronounced anisotropy are favourable for film fibrillation or film cutting techniques.

Polyolefin fibres are hydrophobic, retaining little moisture. They tend to accumulate static charges. However, problems of soiling are kept to a minimum owing to the particular polymer used in the extrusion of the fibre as well as judicious selection of spin finishes.

Isotropic PE fibre has a thermal conductivity of 0.15–0.67 W/(m K), while the crystallinity ratio varies from 0.4 to 0.9. The thermal conductivity of highly oriented PE fibres may attain values higher than 30 W/(m K) above 200 °C. The properties of PE fibres in comparison with those of PP are given in Table 6.7.

The physical and mechanical properties of PE fibres are closely related to its morphology. Lowering the extrusion temperature reduces the crystalline orientation and favours a partial transformation of orthorhombic crystals into monoclinic. Increasing the extrusion temperature and draw ratio is accompanied by an increase in birefringence (Figure 6.8) and crystallinity [6]. An increase in density favours crystallite formation (Figure 6.9).

For higher extrusion temperatures, the annealing effect is favoured and molecular relaxation and recrystallisation are more likely to occur. Because of the variation in crystallinity with increasing draw ratio, tensile strength and modulus significantly increase as a fibrillar structure is formed starting from the spherulitic material. An increase of these properties with molecular weight also occurs.

Studies have indicated that it is appropriate to record not only the overall orientation, as derived from birefringence, but also the crystal orientation, obtainable from X-ray measurements.

Table 6.7 Properties of PE and PP fibres

Property	LDPE	HDPE	PP
Density (kg/m ³)	920	940–970	900–910
Water absorption (%)	0	0	0.03
Dry tenacity (cN/den)	1–3	4–8	6.5–9.0
Wet tenacity (% of dry)	98–100	100	100
Elongation at break (%)	20–60	10–30	18–60
Melting point (°C)	115	135	162–173
Softening point (°C)	100	124–132	149–154
Shrinkage in boiling water after 20 min (%)	10–15	5–10	0–3

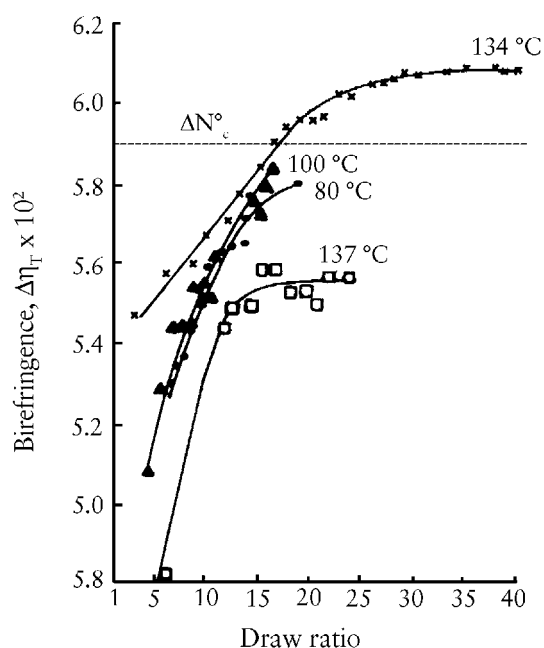


Figure 6.8 Birefringence *versus* draw ratio for ultra-oriented HDPE fibres extruded at 0.23 GPa for various temperatures [6]

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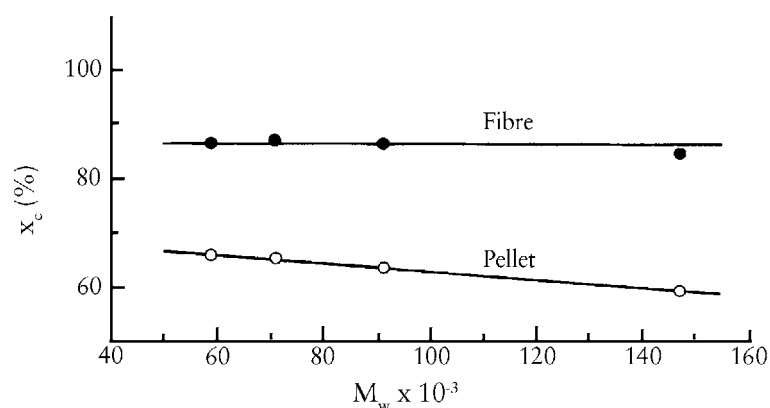


Figure 6.9 Degree of crystallinity *versus* molecular weight for pellets and ultradrawn fibres. The pellets were crystallised by cooling from 147 °C at 20 °C/min [6]

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The results obtained for LDPE and HDPE filaments are presented in **Figure 6.10**. Hadley and co-workers [7] have determined the five independent elastic constants for oriented filaments of polymers, including PE. The orientation was determined in terms of draw ratio and optical birefringence, and explained by aggregate theory (**Figure 6.10** and **Table 6.8**). The mechanical anisotropy induces, by increasing molecular orientation, an increase of transverse Young's modulus E_{11} , measured along the filament axis. This is almost independent of draw ratio for HDPE, while for LDPE it increases significantly.

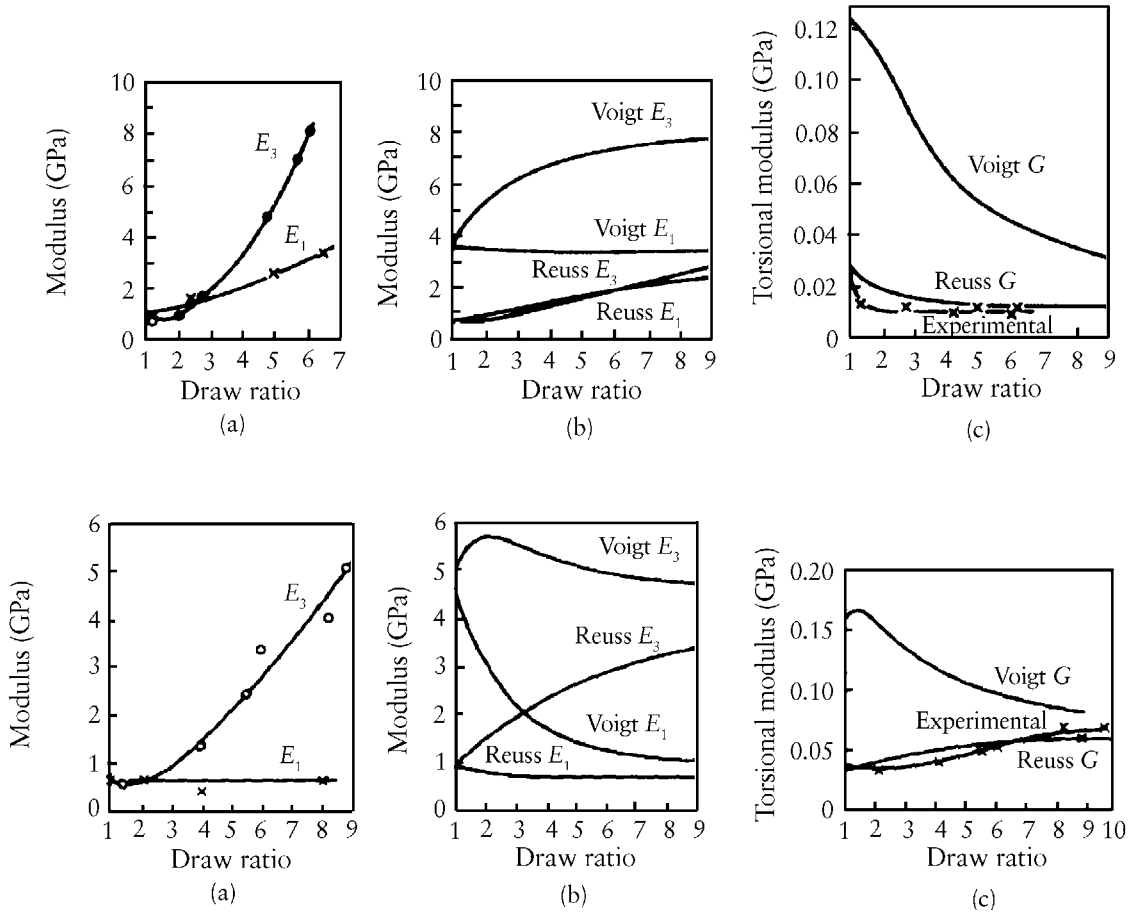


Figure 6.10 (a, b, c) Extensional (E_3) and transverse (E_1) and (c) torsional (G) moduli for LDPE filaments (top) and HDPE filaments (bottom). Comparison between experimental results and simple aggregate theories (Voigt and Reuss compliance are shown) for E_3 , E_1 , and G [8]

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The measured elastic properties for a range of fibres, determined by the ultrasonic immersion method, are given in Table 6.8. It is particularly notable that ν_{12} is greater than 0.5, a result that is in accordance with the fact that, in highly oriented fibres, the high axial stiffness means that transverse compression becomes close to pure shear in the transverse plane.

Fibre type	E_{33} (GPa)	E_{11} (GPa)	ν_{13}	ν_{12}	G_{13} (GPa)
Tenfor polyethylene	57.7	4.68	0.45	0.55	1.63
Dyneema polyethylene	74.3	4.31	0.47	0.57	1.36
Polyethylene terephthalate (PET)	14.9	3.70	0.39	0.65	1.62
Polypropylene (PP)	11.0	2.41	0.39	0.58	1.52
Liquid crystal polymer	97.2	3.24	0.48	0.73	1.30
Standard deviation $\pm 2-3\%$		E_{33}, E_{11} : Young's modulus			
ν_{13} , extensional Poisson's ratio		G_{13} : torsional modulus			

The elastic compliances of some oriented fibres are given in Table 6.9. For PET, HDPE, and PP, $s_{44} \approx s_{11}$; for polyamide, $s_{44} \approx 2s_{11}$. By contrast, LDPE, at least at room temperature, is exceptional, with the extensional compliance s_{33} having the same order of magnitude as the transverse compliance s_{11} , and with the shear compliance s_{44} being more than an order of magnitude higher than either s_{11} or s_{33} . Such measurements provide the basis for the discussion of relaxation transitions.

Material	Birefringence (Δn)	s_{11}	s_{12}	s_{33}	s_{13}	s_{44}
LDPE film 14		22	-15	14	-7	680
LDPE	0.0361	40 ± 4	-25 ± 4	20 ± 2	-11 ± 2	878 ± 56
HDPE	0.0594	15 ± 1	-16 ± 2	2.3 ± 0.3	-0.77 ± 0.3	17 ± 2
PP	0.0220	19 ± 1	-13 ± 2	6.7 ± 0.3	-2.8 ± 1.0	18 ± 1.5
PET	0.1870	16 ± 2	-5.8 ± 0.7	0.71 ± 0.04	-0.31 ± 0.03	14 ± 0.2
Nylon 6.6	0.0570	7.3 ± 0.7	-1.9 ± 0.4	2.4 ± 0.3	-1.1 ± 0.15	15 ± 1

6.5 Compression Moulding

Compression moulding is used for producing items with wall thicknesses larger than 15 mm, which cannot be obtained by extrusion and injection moulding. Compression moulding involves the pressing (squeezing) of a deformable material charged between the two halves of a heated mould, and its transformation into a solid product under the effect of the elevated mould temperature. The temperatures are in the range 140–200 °C and mould pressures vary from 3 to 7 MPa (Table 6.10). The parameters for each step of the operation (melting, preliminary compressing, final compression, and cooling) depend on PE grade (Table 6.11). Compression moulding is used for the manufacture of plates, blocks, fittings, and valves, and machine tools for the textile and electrotechnology industries.

Large UHMWPE sheets are commercially produced using compression moulding. Once the central temperature has reached 180 °C, the mould is slowly cooled to below the polymer crystalline melting point before the mould is opened and the part removed.

	LDPE	MDPE	HDPE
Temperature (°C)	135–175	150–190	150–220
Pressure (MPa)	0.69–5.5	0.69–5.5	3.4–5.5

PE grade	Melting (°C)	Preliminary compression		Final compression			Cooling	
		Pressure (daN/cm ²)	Time (min)	Temperature (°C)	Pressure (daN/cm ²)	Time (min)	Pressure (daN/cm ²)	Temperature (°C)
LDPE	130–140	5–10	15–60	150–160	35	10–12	60–80	30–40
HDPE	150	25–50	30–60	160–200	30	10–20	100–120	50–60

6.6 Sintering and Coating

In sintering, powdery or granular material is compacted by superficial melting with or without external pressure. It is applied for coatings, obtaining semi-finished or end products, and obtaining plates and blocks. Grinding of PE can be carried out both at low and elevated temperatures. Grinding of PE at elevated temperatures is based on its low breaking resistance at temperatures between 60 °C and the melting temperature. For example, the tensile strength is about half that at room temperature. The sizes of PE particles obtained by grinding at elevated temperatures range between 100 and 800 µm. Coatings with PE powders are used for protection against corrosion, for decorative purposes, and as electrical insulation. Sintering is achieved by dip coating in a stationary bed of powder, in a fluidised bed, in an electrostatic field, and by flame spraying.

There are several different types of coating processes, such as dipping, dip forming, spraying, and extrusion. In the most basic coating process, a very fluid plastic paste is spread over a base material or substrate (for example, textile, paper, non-woven fabric). This is then passed through an oven to ensure that the paste forms a gel. In the dipping process, the base material is preheated before being dipped into the plastic. This process is most particularly suited to PVC pastes (emulsion and micro-suspension process), but dry blends (powders) can also be used for specific needs.

When PE is used for extrusion coating, the plastic granules are fed into an extruder where they are melted and homogenised. They are then pumped through a flat die to form a molten sheet which is immediately pressed onto the base material or substrate. The fact that LDPE is easy to extrude, as well as its other characteristics, has made it the most widely used thermoplastic for extrusion coating. It is most often used for coating cardboard, aluminium foil, and PA film. Its most important applications are in liquid packaging, flexible packaging, and photographic paper. In dip coating, powders of PE with uniform dimensions (16 mesh) and MFR of 33–44 or 55–70 g/10 min and EVA copolymers can be used. A fluidised bed procedure is applied both for the inner and outer layer coating of pipe surfaces. In most techniques used the coating thickness increases with time and melting temperature, which varies from 300 to 360 °C.

Layers made from coloured PE used for decoration purposes must be very thin, often below 0.05 mm, usually having a thickness of 0.025 mm. Most often LDPE with an MFR of 17–20 g/10 min is used. It ensures a transparent, smooth, and glossy film, mainly due to the ease of fusion of the particles. Smooth films from LDPE of high viscosity are quite difficult to obtain, whereas use of low melt viscosity polymer can cause difficulties in obtaining continuous film. LDPE coatings are used within the temperature range –10 to +90 °C for long-term use and at temperatures higher than 90 °C for shorter use times. HDPE is easily available in powdery form. However, its high melt viscosity prevents one obtaining translucent and smooth films – only matt translucent coatings are obtainable. Thick films are necessary to avoid pore formation. HDPE films are expensive: as such they are recommended only for decorative purposes. They can also be used for protective coatings. They are safely used at temperatures of around 100 °C. The abrasion resistance and chemical resistance of HDPE are superior to those of LDPE. In some cases a 40HDPE/60LDPE mixture is recommended. XPE powders may be deposited as coatings in a fluidised bed process or by flame spraying.

The applications of materials produced using the sintering technique are wire baskets, trays, door accessories, clips, books, clamps, metal containers and tanks for corrosive liquids and pastes, metal fittings used in joining with PE and other plastics, stirring equipment used in chemical laboratories and industry, and many others.

To produce plates and blocks by sintering, a polymer powder is compacted under a pressure of 100–150 daN/cm² for 5–10 minutes at room temperature, or after preheating in a fluidised bed. The preform thus obtained is pressed at 30–50 daN/cm² at 180–220 °C depending on the thickness of the material layer. Cooling is performed after the pressure has been increased to 200 daN/cm² to compensate for the volume contraction and to ensure that the plate is flat. Pressure is maintained to a temperature of 50–60 °C, whereupon the plate is removed. Pressure, temperature, and pressing

time determine the uniformity of PE particle sintering but mode and rate of cooling are fundamental for the plate characteristics. XPE is also suitable for such processing. The finished articles are in their final shape and can be rigid or soft, compact or cellular.

Injection blow moulding allows hollow articles to be produced. With overmoulding (co-injection), it is possible to produce articles with rigid cores (metal or polymer) by placing the cores in the mould before the plastic is injected.

6.7 Thermoforming and Vacuum Forming

Thermoforming involves the heating of a flat thermoplastic sheet to a softened state (above the glass transition temperature or near the melting temperature) followed by the deformation (forming) of the softened sheet into the desired shape by pneumatic or mechanical means, and finally its solidification (freezing) into this shape by cooling. In its most sophisticated form, thermoforming can provide small tolerances, sharp detail, and meet very stringent specifications. When advanced finishing techniques are used, high-technology thermoforming can match the results obtained by injection moulding. Thermoforming is particularly suitable for producing large panels, housings, enclosures, and similar parts. The formed parts can be trimmed by various techniques.

Thermoforming may be achieved by mechanical forming, vacuum forming, pressure forming, or various combinations of these. Mechanical forming is applied mainly to PP. The low elasticity of semi-crystalline polymers at forming temperatures makes vacuum forming very difficult. It is also difficult because the tensile strength varies with temperature, especially below the crystalline melting temperature. The melt strength and strain hardening are depressed by a processing history in a single-screw extruder, whereas reprocessing by a two-roll mill enhances the melt strength again.

Thermoforming of polyolefins raises some specific problems because of their low thermal conductivity and high heat capacity and crystallisation heat which lead to longer thermoforming cycles. The increase of the thermoforming cycle is mainly due to the heating step, which depends, in its turn, on the sheet thickness, heating temperature, temperature of the heater, and distance at which the heater is placed. To avoid deformation of the sheet, it is necessary to heat both its sides. In the case of an extruder-integrated installation, the sheet is supported by a textile or a metallic band. Non-uniform distribution of the radiant energy on the sheet surface causes local non-uniformities in the thickness of the walls of the formed part. This must be avoided, especially with items having a high draw ratio.

Sheets of HDPE are frequently subjected to thermoforming processing to obtain sports goods, products for the automotive industry, and others. HDPE with a density of 0.960 g/cm^3 and MFR of $0.1\text{--}0.15 \text{ g/10 min}$ is ideal for thermoforming because it has a long sag when heated and the impact strength in the finished part is high. LDPE is also manufactured in sheet form. However, applications in thermoforming are limited because of its low modulus. EVA copolymers (5–10% VA) are used to take advantage of their high elongation and rubbery nature.

6.8 Rotational Moulding and Transfer Moulding

6.8.1 Rotational Moulding

The relatively low heat conductivity of PE is associated with slow rate of thickness build-up, and the tumbling action in rotational moulding only ensures that the powder is regularly brought in contact with the forming polymer shell. When the whole material is fed, further heating may help consolidate and homogenise the material, through intermolecular diffusion in particular, also producing a smoother inner layer.

Rotational moulding or rotomoulding is an extremely popular and much used process for producing items that are usually hollow. It is most often used for very large articles that are usually made in small quantities. Items such as children's toys, garden furniture, and road traffic bollards are manufactured by rotational moulding.

In rotational moulding a fine powder of plastic is fed into a metallic mould which after being closed is rotated around both the equatorial and polar axes and concomitantly the mould is heated at a temperature above the melting point of the polymer. The melt is flung to the walls of the mould by centrifugal force where it forms a skin. After the plastic melt has covered the entire inner surface of the mould the whole aggregate is cooled at room temperature. The cooling is carefully controlled to avoid the product shrinking or warping. The mould is opened and the product is removed.

Using rotational moulding one can obtain products with large volume ranging from tiny ear syringes to 10,000-litre storage tanks. For PE products with wall thickness between 1.6 and 4.8 mm a heating time of 7–15 minutes is recommended. Desirable particle sizes between 35 and 75 mesh are optimum for good transfer and from the fluid flow point of view.

When PE is subjected to rotational moulding, warpage can occur due to the operational conditions. Warpage is a complex process depending on mould size, material from which the mould is constructed, cooling mode, and presence or absence of release agent.

XPE can be rotational moulded to produce automotive parts, toys, food handling systems, and chemical tanks. It also provides higher heat/chemical resistance and stiffness than normally achieved by rotational mouldable LLDPE. LDPE with an MFR of 2–20 g/10 min and a density of 916–939 kg/m³ is recommended, followed by EVA copolymer and HDPE. HDPE is more difficult to melt than LDPE. It also shows a tendency to thermal degradation and more pronounced deformation on cooling, mainly for flat surfaces. PP is avoided because of its susceptibility to degradation.

Apart from products with compact walls made of a single type of polyolefin, rotational moulding can be also used to obtain products with cellular and stratified walls made from PE/PP, PE/PA, etc.

6.8.2 Transfer Moulding

Transfer moulding is a process in which molten resin is transferred from a melt pot into a mould that is hotter than the resin. This is unlike injection moulding where the mould is cooler. The higher temperature is important for filling long moulds to maintain a consistent wall thickness and to compensate for shrinkage. Once the plastic has cooled, it is removed and the next charge is loaded.

6.9 Casting

Centrifugal casting is used to obtain non-normalised pipes, especially pipes with large diameters, which cannot be formed by extrusion. Solid granulated PE is charged into a horizontal cylindrical metallic mould, which is externally heated and rotated on its longitudinal axis. Melted PE forms a viscous fluid, which, under the action of centrifugal forces, is shaped by the mould walls. After cooling of the rotating device a pipe of uniform wall thickness is obtained.

The mechanical properties of cast pipes are generally inferior to those of extruded pipes. However, using grades of PE containing antioxidants and carbon black it is possible to produce cast pipes with mechanical properties closely approaching those of extruded pipes.

6.10 Recycling and Recyclates

At the end of their useful life, waste polymers enter waste streams as either post-consumer waste or industrial scrap. Households and the distribution industry sector are sources of the former while the latter arises from processing, filling, assembling, installing, and polymerisation. Much of the industrial waste is recycled within the process and the rest is usually sent for reprocessing by a third party. Consequently, little of this material is discarded as waste. The majority of post-consumer plastic waste, however, reaches the environment and hence the emphasis in polymer waste management is on this type of waste stream.

Three options are available for recycling: mechanical recycling, chemical recycling, and energy recovery. Mechanical recycling uses physical means such as grinding, heating, and extruding to process waste plastics into new products. Chemical recycling uses chemical processes to convert waste into useful products, such as monomers for new plastics, fuels, or basic chemicals for general chemical production. These two options are often referred to as material recycling. The third recycling option, energy recovery, generates heat or electricity (or both) either by direct incineration, for example, in municipal incinerators, or by replacing other fuels (in blast furnaces, cement kilns, or power stations).

Very costly operations are necessary before recycling, namely, collection, sorting and separation. Separation of different polymers is particularly important for mechanical recycling; mixed materials produce recyclates of low quality, which can be used in only a limited number of applications. Hence, mechanical recycling is really best suited to clean plastic waste, such as packaging material. Each separated plastic material is ground, washed, and dried. New products are obtained by extrusion and other techniques. Recyclates may be upgraded by addition of fillers, fibres, stabilisers, pigments, flowing aids and others.

Because of the ease of processing, most products made from PE can be reprocessed as other products, these being known as secondary use. As can be seen from Table 1.3, one of the primary uses of HDPE is to make bottles for milk, water, juices, bleach, detergents, motor oil and so forth. For more than 20 years, HDPE has been the preferred material for drinking water and sewerage pipes. Nowadays it is also used for gas pipes. The manufacture of HDPE packaging film is growing rapidly and HDPE currently makes up around 21% of the packaging market. Recycled products made from HDPE include detergent and engine oil bottles, dustbins, soft drink bottle crates, drainage pipes, animal pens, drums, matting, milk bottle carriers, industrial pallets, plastic lumber, traffic barrier cones, flower pots, golf bag liners, kitchen drain boards, and hair combs.

LDPE is widely used in applications requiring clarity and ease of processing. Its most common use is as film (73%) for sacks, shrink wrap, stretch wrap, and refuse bags. LDPE is the predominant material for telecommunications cables and forms a water vapour resistant seal in the lamination of co-extruded multilayer films. When recycled, LDPE can be used to make most of the products made from virgin LDPE (except for packaging).

Chemical recycling includes gasification, hydrogenation, and pyrolysis (thermolysis) [1, 9, 10]. The main objective of the degradation/decomposition procedures for feedstock preparation processes is to convert the long-chain polymers into smaller hydrocarbon chains that can be readily processed in existing industrial equipment. The level of metals, halogens (mainly chlorine), and nitrogen are also very important for use as high-value refinery or petrochemical feedstocks. At present such recycling, of course, depends upon economics, but the driving force is primarily environmental.

It is known that polyolefinic polymers can be readily thermally decomposed to gaseous and liquid hydrocarbons. The pyrolysis of these kinds of polymers in an inert atmosphere or under vacuum at elevated temperatures gives heavy hydrocarbons as major reaction products. Mainly light paraffins and olefins are obtained during polymer thermolysis at higher temperatures (above 700 °C). In

the free radical degradation mechanism of the polymer chain proposed to explain the patterns of pyrolysates, it is assumed that the degradation of polymers is a chain reaction involving thermal initiation, depropagation, intra- and inter-molecular transfer, and termination of radicals.

Degradative extrusion is a way of preparing commingled plastic scrap for chemical material recycling which allows highly diverse mixed plastics to be homogenised, sterilised, compacted, chemically modified, dehalogenated, and converted into a form suitable for transport. The processed plastic wastes can be safely stored or used. The process may be used to obtain end products such as gasoline, waxes and fuels. During the degradative extrusion process, a reduction in molecular weight under thermal mechanical work and chemical agents takes place. Chemical agents such as air, oxygen, steam, hydrogen and degradation-promoting additives, and metal oxides and other catalysts are added to the feedstock or fed into the barrel of the extruder to facilitate degradation. As a result a homogeneous liquid melt, granulated solid, or gas (above 500 °C) are obtained. The process is carried out in both cascade extruders or in single-line co-rotating and/or counter-rotating twin-screw extruders. Melt viscosities depend on degradation temperature, shear stress, and residence time. Degraded extrudate can be mixed with crude oil residue in certain proportions, the mixtures showing adequate stability of properties.

Low-temperature pyrolysis or cracking of plastic waste gives high-boiling liquids or waxes as potential feedstocks for steam cracking or fluid-bed catalytic cracking (FCC) processes currently used to produce olefins for polymerisation. The problem of technological utilisation of polyolefin waste is of great importance when considered economically and ecologically. The importance arises from both the valuable products obtained and the enormous quantity of waste resulting from synthesis, processing, and domestic and industrial consumption. The maximum yield of product suitable for recycling as a petrochemical feedstock requires temperatures in the range 400–600 °C together with a tailored residence time to minimise over-cracking and coke production. Under these conditions the yield of light gas can be limited to that required for process heat (10–15%). Waxes obtained from polyolefin waste can be further steam cracked resulting in monomers (ethylene and propylene, 20–40%), methane (10–14%), and gasoline and liquids as the main products.

Thermochemical processes used to recycle the feedstock from plastic waste are usually those used in the petrochemical industry. These include visbreaking (viscosity reduction or breaking), steam cracking,

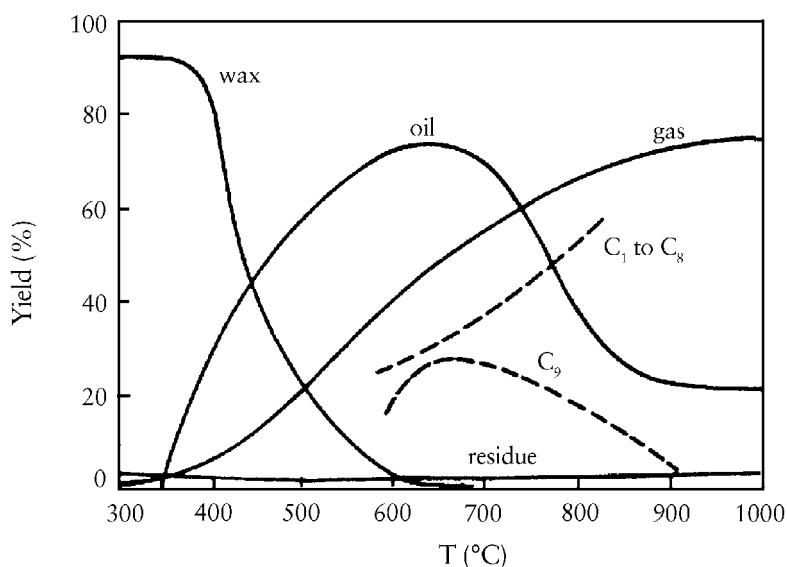


Figure 6.11 Formalised curves (solid lines) of the variation of the yield of global pyrolysis products with temperature of pyrolysis and some examples for certain products (dashed lines) [1]

catalytic cracking, liquid- and gas-phase hydrogenation, pyrolysis, coking, and gasification. The yield of waxy, liquid, and gaseous products depends on the working conditions such as heating rate, temperature (Figure 6.11), gas flow, residence time, type of reactor, and mode of heat supply. Moreover, it is possible to control the properties of each pyrolysis product by changing the reaction conditions, for example, the molecular weight and MWD of waxes, boiling points of liquids, and composition of gases.

Polyolefinic materials like PE and PP contain approximately 14 wt% hydrogen. These materials could provide hydrogen during thermal co-processing with wood biomass and could lead to an increase of liquid production. There are some data indicating that mixtures of wood with PE and PP can be successfully converted into liquids using pyrolysis and hydrolysis techniques [11]. Mixtures of commercially available MDPE ($M_n = 20,000$), atactic PP (aPP), and isotactic PP (iPP) with different amounts of wood biomass (1:1 weight ratio, biomass/plastic) have been investigated [12]. It is found that the chemical composition and structure of the polymers have a significant influence on the distribution of products in biomass/plastic co-pyrolysis. At 400 °C, the maximum yield of both light and heavy liquids is recorded. At this temperature, the most important parameter for liquid production, especially for the light fraction, is the biomass/plastic ratio in the feedstock. The yields of light liquids from beech/plastic mixtures decrease in the following sequence: iPP > aPP > MDPE. The yields of heavy liquids increase in the same order. It can be concluded that the lowest yield of light liquids is obtained from a mixture of biomass with the most thermally stable polymer.

Using the peak property method in order to estimate the pyrolysis kinetics of HDPE, Kim and co-workers found that random scission degradation, which is expected to be a major decomposition mechanism of HDPE, does not follow first-order kinetics rigorously [13].

Energy recovery from waste by incineration is a very controversial issue. It has a low degree of acceptance due to environmental pollution and corrosion problems. Polymer wastes, particularly polyolefin ones, have a high calorific value of 36–46 MJ/kg. Hence they will give an important contribution to reducing the energetic needs in the production of hot water, steam, electricity, etc.

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7 Considerations of Product Design and Development

7.1 Introduction

Designers have a valuable role to play in ecodesign because of their involvement at the early stages of the product development process, where the design brief is most flexible and the most critical decisions are made with respect to cost, appearance, materials selection, innovation, performance, environmental impact, and perceptions of quality (longevity, durability, repairability) [1]. The design of a polymeric product for a specific application is a complex task. This is particularly true in the case of polyethylene (PE), which exists in a great variety of material forms and many processing methods are available for it.

When a product is needed for a specific application, it has to meet several requirements, sometimes termed 'constraints', which can be divided into three categories: geometric constraints, property constraints, and economic constraints [2]. Geometric constraints involve the shape and dimensions of products and may be dictated by aesthetic, functional, and other factors. Property constraints are associated with material characteristics and environments (loads, chemicals, and others). Economic constraints correspond to the cost limits and they are closely related to the volume of production.

The design of a PE-based product normally results in the specification of a geometry for the product (shape and dimensions), a material choice (commercially available grades with specifications; see **Table 3.8** for the properties of various PE types), and a process equipment choice (commercially available equipment fitted with product-specific tool). The three constraints are interdependent in a product design so that the design procedure must be an iterative process. A strict property constraint may be imposed on the material and, as a consequence, the process, while a less stringent property constraint may offer alternatives. For example, in the case of a narrow-neck bottle, a strict geometric constraint may impose a choice between extrusion blow moulding and injection blow moulding, blow moulding being the preferred one. In the case of a wide-neck jar, injection moulding may be a viable alternative. It is always preferable for product designers to collaborate closely with tool designers. For example, changes in shape could be made that do not affect the functional role of a product but that considerably reduce the complexity of a tool and thus the cost and reliability.

Property constraints for a given application are generally multiple. This is why it is important to distinguish between primary property constraints, which must be met for a certain performance level, and certain secondary property constraints, for which some 'trade-off' may be acceptable. Different economic constraints coupled with similar geometry and property constraints may dictate different processes associated with the same generic material but very different grades, for example, small production run snowmobile gas tank/rotational moulding (RM grades of PE) or large production run tank blow moulding (BM grades of PE). Material price and the process operation cost directly affect the product cost, while the tool price influences it only indirectly.

Product design requires access to handbooks and other data sources to obtain information about all properties of the materials used. The development of computer databases of commercial polymers with their properties, processing conditions, and known applications has had a profound effect on the procedure of product design. In this case a vast amount of information can be scanned rapidly to yield at least a preliminary selection of candidate materials and processes. The scanning can be automated if the constraints are specified in an appropriate manner. The mechanical design of a part is another area where computers are increasingly being used. Besides the commercial geometric definition of parts (computer-aided drafting), the distribution of stresses in a loaded part can be determined through finite element analysis, leading to an optimisation of shape and dimensions (computer-aided design).

7.2 Material Selection

The ultimate purpose of all polymer technologies is the production of objects with the properties required by design, specifications, and usage; costs are an additional limiting factor. The type of resin and the processing method are the two possible variables, which are considerably dependent on each other, however, a choice of one narrows the choice of the other, although usually more than one combination is capable of achieving a given purpose. PE, available in a wide range of densities, with each density produced in a wide range of melt indices, provide a broad spectrum of available resins, supplemented by modified resins, block and graft copolymers, blends, and composites. Composites can be even more closely tailored to provide very specific property combinations for very specific applications.

Therefore, considerable knowledge and understanding of the entire field is required to make the best choice of resin and processing method for a particular purpose. No generally useful rules can be given, only a few remarks as follows. Processing procedures are particular in requiring a resin of a certain melt index range. Resins with a high melt flow rate (MFR) are needed for coating and injection moulding. Extrusion moulding is best done with polymers of high to medium MFR. PE with a low MFR is used for blow moulding, pipe and filament extrusion, and wire coating. Resins for other applications, such as film or moulding, may cover a wide MFR range. Some correlations between PE grade characteristics and uses are given in Table 7.1.

Some correlations between material choice and properties are shown in Figure 7.1.

Table 7.1 Correlations between PE grade characteristics and uses		
Grade	Melt flow rate (g/10 min)	Density (kg/m ³)
High-density polyethylene		
Pipe	0.1–0.45	938–955
Blow moulding copolymer	0.2–0.45	950–957
Blow moulding homopolymer	0.5–0.9	960–963
Extrusion	0.1–0.55	940–965
Film copolymer	0.2–0.38	937–942
Film copolymer	0.35–0.6	943–949
Injection moulding copolymer	3–60	945–957
Injection moulding homopolymer	4–30	959–965
Low-density polyethylene		
Blow moulding	1–3	917–924
Blow moulding, low levels of VA	1–3	917–924
Extrusion	0.8–3	915–925
Extrusion, 1–3% VA	0.8–3	915–925
Injection moulding	6–40	915–925
Low-density polyethylene copolymer		
EVA, 1–33% VA	0.7–250	
EMA, 3–30% MA	2–35	
Linear low-density polyethylene		
Film/extrusion, butene	0.6–3	913–922
Film/butene, various levels of slip	0.6–3	913–922
Film/extrusion, hexene	0.6–3	913–922
Film/hexane, various levels of slip	0.6–3	918–929
Injection	6–60	919–925
EMA: ethylene–methacrylic acid MA: methacrylic acid	EVA: ethylene–vinyl acetate VA: vinyl acetate	

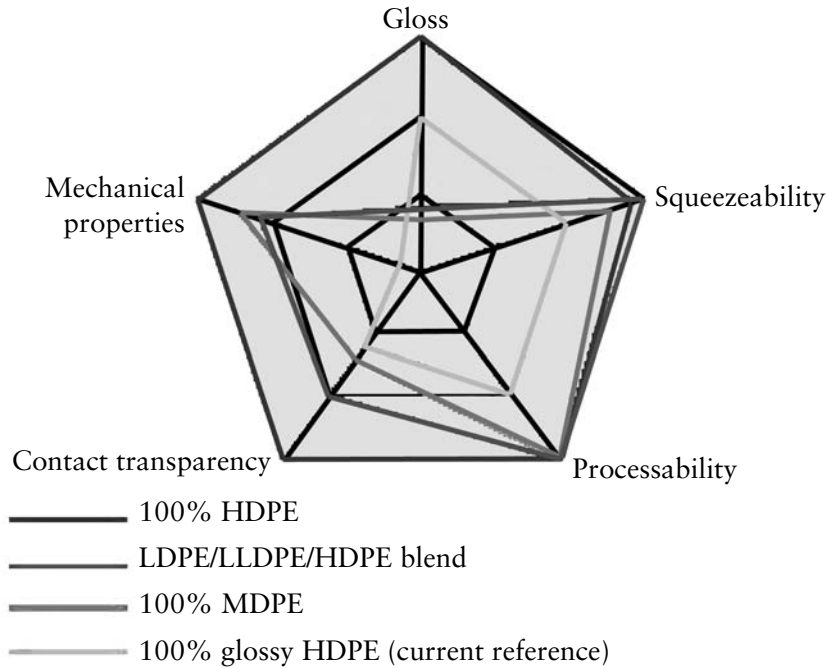


Figure 7.1 Correlations between properties and types of PE

Source: Atofina papers, 2002. Copyright Atofina 2002.

The selection of the grade for each application and the corresponding processing technique is made according to the advantages and disadvantages of each type of PE grade or product characteristics [3].

- High-density PE (HDPE) offers very low cost, excellent chemical resistance, very good processability, good low temperature resistance, excellent electrical insulating properties, and very low water absorption. Also, it is US Food and Drug Administration (FDA) compliant. It is susceptible to stress cracking, has lower stiffness than polypropylene (PP), shows high mould shrinkage, has poor UV resistance, has low heat resistance, and high-frequency welding and joining are impossible. HDPE can be processed very easily by injection moulding, extrusion (tubes, blow and cast films, cables), blow moulding, rotomoulding, and so on.
- Low-density PE (LDPE) also has very low cost, excellent chemical resistance, very good processability, high impact strength at low temperatures, excellent electrical insulating properties, and very low water absorption, is FDA compliant, and can be transparent in thin-film form. It is similar to HDPE, in that it is susceptible to environmental stress cracking, exhibits low strength, stiffness, and maximum service temperature, has high gas permeability (particularly to carbon dioxide), has poor UV resistance, and is highly flammable. High-frequency welding and joining are impossible. The most common process used for LDPE is extrusion (tubes, blow and cast films, cables). LDPE can also be processed by injection moulding or rotomoulding.
- Linear low-density PE (LLDPE) offers, besides the advantages mentioned for LDPE, higher tensile strength, higher impact and puncture resistance, and lower-thickness films can be blown compared to LDPE. Its disadvantages are that it has a lower gloss, narrower temperature range for heat sealing, and poorer processability than LDPE. The most common process used for LLDPE is extrusion (tubes, blow and cast films, cables). LLDPE can also be processed by injection moulding or rotomoulding.
- Ultra-high molecular weight PE (UHMWPE) has several differences compared with other PE types, such as higher notched impact strength, higher wear resistance, higher energy absorption

capacity at high stress rates, higher heat deflection temperature, higher stress crack resistance, and very low water absorption. It is also FDA compliant. However, UHMWPE is not melt processable because of its extremely high viscosity and it is of higher cost than other types of PE. It can be processed only by ram extrusion and compression moulding.

- PE with 30% glass fibre has higher stiffness and slightly higher toughness than HDPE. Other advantages are similar to those of other PE types, such as very low cost, excellent chemical resistance, very good processability, good low temperature resistance, excellent fuel resistance, excellent electrical insulating properties, and very low water absorption. It is FDA compliant. A disadvantage is it has poorer processability than HDPE. It can be processed by rotomoulding and injection moulding.
- Crosslinked PE (XPE) offers higher stiffness and heat resistance, reduced creep, and reduced sensitivity to stress cracking compared to HDPE. It has good low-temperature resistance, good electrical insulating properties, and very low water absorption. The disadvantages are the higher cost than HDPE, peroxide crosslinking can affect its electrical properties, it exhibits poor UV resistance, and high-frequency welding and joining are impossible. XPE can be processed under similar conditions to standard HDPE pipe grades.

7.3 Processing Techniques

Commodity PE can be processed by various methods, which rank in importance and increasing PE molecular weight as follows.

- Injection moulding is used for PE with high MFR (low viscosity) and narrow molecular weight distribution (MWD). The viscous resin is squirted by means of a plunger out of a heated cylinder into a water-chilled mould, where it is cooled before removal. Processing is performed at around 170–300 °C, depending on the material, but decomposition begins above 310 °C (and very short processing times are required beyond this temperature). PE does undergo some degree of shrinkage during injection moulding (LDPE 1.5–3% and HDPE 2–4%). Injection moulding is used to produce a wide variety of domestic and industrial items, which are too numerous to be listed.
- Extrusion in which melted PE is extruded at 160–240 °C is used to produce pipes using single- or twin-screw extruders. With mould temperatures of up to 300 °C, extrusion is used to produce film, sheeting, and monofilaments.
- Compression moulding uses powder or granules of semi-finished product put directly between tool faces. The faces are brought together under pressure and the material is shaped.

7.3.1 Extrusion

The shaping tool associated with extrusion is usually called a die. Widely different die designs are associated with filaments, profile products, tubes or pipes, and films or sheets. Filaments are often made from plate dies featuring multiple orifices with streamlined (tapered) entrances. Profiles without hollow sections are made from plate dies. For ease of wire covering and extrusion covering, a die mounted with its extrusion axis perpendicular to the extruder axis (crosshead die) comprises a tapered guider or core tube for the substrate, and a suitable channel to direct the covering fluid polymer from the extruder exit to an annular gap between a bushing and the continuously moving substrate. The formation of a hollow extrudate, such as a tube or a pipe, requires the use of a mandrel to form the inner surface, while a bushing forms the outer surface. There are several possible slot (slit) die configurations for the formation of films or sheets. T-shape dies feature a simple circular manifold that channels the material sideways from the feed zone, after which it flows axially through the intermediate pre-land and land. Coat-hanger dies feature a slanted, teardrop-shaped manifold to

minimise material hold-up or stagnation. In some cases, complex fishtail dies have been designed for a gradual flow transition from a circular cross-section at the extruder exit to a thin rectangular cross-section at the die exit. It is very difficult to design and build a film or sheet die that will give a uniform product thickness across the entire width. To adjust the gap thickness in operation, two types of devices are used: choke bars and flexible lips.

In general, the design of extrusion dies is complicated by the phenomenon of die swell, which is very pronounced for most polymeric materials. Die swell, which may involve a two- or three-fold increase in cross-sectional dimensions, depends on resin characteristics as well as on flow conditions. For simple geometries, drawdown can be used to correct the dimensions, but this is not generally sufficient for complex shapes such as those encountered in profiles.

Extrusion outputs are sometimes limited by flow instabilities producing rough surfaces (shark skin) or periodic fluctuation, but the cooling of thick extrudates is often the major limiting factor because of the low thermal conductivity of PE.

Although the die is the major element in the formation of an extruded product, downstream auxiliaries are often essential to meet product specifications, while maximising the output. Auxiliaries include cooling, sizing, post-forming, and haul-off, as well as cutting and/or winding devices. Cooling of the extrudate is often the limiting factor for extrudate speed. This is related to the low thermal conductivity of PE and problems associated with the formation of a solid skin and subsequent shrinkage of the inner material. Sizing depends strongly on the shape and dimensional specifications of the products. In the case of tubes and pipes, for example, if the external diameter is crucial, the emerging tubing is forced against an external sleeve or a ring-like sizing jig, or by internal pressure. If the internal diameter is important, an internally cooled mandrel-like sizing jig, in combination with internal vacuum, may be used. In both cases the thickness can be controlled through the amount of axial pull (drawdown). The thickness of sheets and films may also be controlled by the amount of drawdown, while that of extruded sheets, pipes, and other materials can be monitored continuously with a variety of gauges (nuclear, infrared, ultrasonic, magnetic). Flexible extrudates may be wound, while rigid ones may be cut to length by fly cutters, featuring fast-rotating blades or knives, or by travelling cut-off circular saws, which follow the extrudate during cutting sequences.

Practically all PE grades can be processed by extrusion, but in order for the emerging extrudates to maintain their shape until they solidify, extrusion grades tend to have relatively high molecular weights associated with high viscosity and melt strength. Very viscous UHMWPE is often processed by screwless (ram) extrusion.

Extruded tubular products can range in size from tiny tubing, used for separation purposes or drinking straws, to pipes as large as 1.6 m in diameter and 2 cm thick. They are made of HDPE. Typical production speeds for intermediate sizes are about 1–13 m/min for rigid pipes and about 10–20 m/min for flexible ones. Typical large outputs are about 1000 kg/h. Stiff, but light, pipes are made by coextrusion with cellular (foam) cores. Very large tubes are made with corrugations produced in a post-forming operation. Very large tubes are made by helically winding, and then bonding or mechanically interlocking a suitable extruded profile, a method that does not require a very costly investment. Flexible reinforced tubing is made by extruding an inner liner, braiding around it a fibre reinforcement, and subsequently extruding over it a cover (jacket). LDPE or HDPE (and also polyvinyl chloride) are widely used for tubing or pipes. For flat products (films of 0.25 mm and sheets of thickness >0.25 mm), production speeds can vary from 450 m/min to 15–30 m/min, decreasing with increasing thickness. Corrugated sheets featuring high longitudinal rigidity are made by a post-forming operation. Production speeds for wire and cable coating reach 3000 m/min or 175 km/h.

Melt temperatures for extrusion of HDPE are 200–300 °C and for LDPE are 180–240 °C. Higher melt temperatures are needed for extrusion coating (280–310 °C). A three-zone screw with a length-

to-diameter ratio (L/D) of around 25 is recommended. Recommended melt temperatures for LLDPE extrusion are 205–260 °C. XPE can be processed under similar conditions to standard HDPE pipe grades. Recommended extrusion conditions are screws with a L/D ratio of at least 25 and a melt temperature of about 190 °C.

7.3.2 Film Blowing

In film blowing it is essential to achieve excellent uniformity of the gap thickness and flow rate around the entire die circumference, as well as to minimise material inhomogeneity for very sophisticated designs. Crosshead dies of the bottom-fed/spider type tend to cause problems with weld lines, while it is difficult to obtain flow rate uniformity with side-fed/spiderless types. Modern film-blowing dies are increasingly of the bottom-fed/spiral mandrel type. In order to distribute across the width of the final wound product the inevitable circumferential thickness variations in the extruded tube or the blown bubble, a slow continuous or oscillatory rotation of the mandrel, the bushing, the entire die, and even the haul-off tower must be used.

All PE grades (LDPE, LLDPE, high molecular weight PE (HMWPE)/HDPE, and others) are commonly used as film-blowing resins. Heavy-duty films are often in the range 0.1–0.2 mm and can be as thick as 0.5 mm. They are used for agricultural, construction, and industrial applications, including covers for silage, greenhouses, chemical/solar ponds, flat cars, or liners for reservoirs, ponds, pits, and ditches, and are often associated with irrigation. Packaging and agricultural mulch film applications are also increasingly used. Multilayered (multiple) coextruded blow films, which contain from 3 to 11 layers, are increasingly used for barrier packaging. Blow films can produce a moderate amount of heat-induced contraction (about 50%) and thus find applications as shrink films. Linear production speeds are in the range 10–45 m/min and can even be 200 m/min for thin products such as garment bags.

7.3.3 Thermoforming

Thermoforming transforms a flat sheet (blank), of uniform thickness, into a contoured product of variable thickness resulting from nonuniform biaxial stretching. At any stage of the forming process, most sheet deformation takes place in areas that have not yet come in contact with the cold tool. For a typical cup-like product, regions such as the edge, the side, the corner, the bottom, the apex, and the flange have thicknesses that can be substantially less than that of the blank or web. The material also retains a high degree of biaxial orientation, which may have a positive effect on properties. The severity of deformation is often characterised by a drawdown. A number of techniques and variations are used to make products that can combine high drawdown ratios with acceptable thickness distributions, such as pneumatically and/or mechanically induced deformations. Pneumatic deformation is most commonly done by vacuum (suction), thus with a maximum pressure differential of about 0.1 MPa, surge tanks are normally used to permit fast evacuation rates. Positive air pressure can be helpful for thick products or to reproduce fine tool surface textures. Mechanical deformation tends to be used primarily for pre-forming or pre-stretching before final vacuum or air-pressure forming.

The equipment used to thermoform parts depends very much on the size of the parts and the rate of production desired. Thermoforming tools are one-surface tools. When the important product surface is not that much in contact, the surface does not require a good finish. For materials like PE and PP a sand (grit)-blasted tool surface facilitates complete air evacuation. The extraction of products from tools requires a larger taper ($\sim 5^\circ$) for positive tools than for negative tools ($\sim 2^\circ$) because of material shrinkage. Small corner radii are generally difficult to form or cause excessive thinning. Crystallising olefins are occasionally used requiring accurate control of blank temperature. The thermoderformability of thermoplastics is often associated with their melt strength. The requirements are a good resistance of the melt to low stresses but high extendability under higher stresses (forming stage).

Small products are made in high-output machines, often of the roll-fed, in-line type, using multicavity tools that are used for packaging and disposable items for food and medical applications (skin and blister packs, individual containers for jelly or cream, vials, cups, tubes, trays, and lids). Millions of parts per day can be produced with a single tool featuring several cavities. Small and medium-sized products can have relatively complex shapes, the use of refined techniques allowing a reasonable control of increasing thickness. Large parts normally have relatively simple shapes corresponding to moderate drawdowns and are generally made by a basic technique.

7.3.4 Blow Moulding

Tooling for a specific extrusion blow moulded product involves a mould as well a die to produce the parison. In the case of injection blow moulding, an injection mould is needed for the preform in addition to the blow mould. Parison extrusion dies feature a 90° configuration, and feed sections are designed to minimise the formation of weld lines. Blow moulds are subjected to moderate pressure and clamping forces compared to injection moulds; they can thus be constructed more lightly, and aluminium (cast or machined) is often used because of the advantages of weight saving and heat conductivity. Steel is preferred for high-volume moulds. Depending on the product shape, moulds may feature side cores, eye-forming handle sections, and off-centre neck-forming sections with puncturing blow pins or needles.

For crystallising resins such as PE, the process of blow moulding requires good stretchability of the softened thermoplastic (melt strength) over a reasonable temperature ‘window’ and high molecular weight, so that HMWPE is by far the most widely used resin for large products. PP tends to be used in processes that promote orientation, such as stretch blow moulding, and where a higher temperature resistance is required.

Blow-moulded products are associated with certain inherent limitations concerning shapes and wall thickness. While the blow-moulding process normally yields one-piece, closed, hollow products, pairs of open, hollow products have been made by splitting closed mouldings.

Production lines are sometimes dedicated to a single large-volume product, or versatile machines are used for the custom production of suitable parts. Shipping drums are produced at a rate of about 20 per hour in one-cavity machines. They often have stiffened annular ribs as well as lifting rings to allow ‘parrot beak’ handling and bung closure elements, which are sometimes injection moulded separately and incorporated during blow moulding. Stationary storage items blow moulded from PE are now made in volumes as large as 10,000 litres, their uses including underground residential fuel oil storage and septic tanks. Mandrel forms for filament winding of pressure tanks and solid fuel rocket cases, ducts, and bellows and double-walled housing are other industrial applications of blow moulding. In the automotive industry blow moulded parts include disposable containers, disposable windscreen washer fluid canisters with handles, portable gas canisters with handles, brake fluid reservoirs, liquid coolant overflow tanks, and HDPE fuel tanks produced in about three minute cycles. Also, various toys are made by the blow moulding of HDPE.

7.3.5 Rotational Moulding

Moulds for rotational moulding are normally split negative moulds with built-up mechanical locking. The need for rapid heat transfer and minimum weight to facilitate rotation calls for relatively thin walls, which are possible in view of the low pressure involved. Large moulds are fabricated from steel in sheet form with a thickness in the range 1–3 mm. External reinforcing frames are used. Small moulds are made from aluminium with a thickness of around 6 mm. A modest degree of internal pressurisation improves the dimensional accuracy of parts. The nature of the process normally needs the use of a relatively thin powder of 200–500 µm. Particles featuring sharp edges and corners process better than purely spherical ones. The ‘running’ properties of the powders and the build-up

of electrostatic charges are among the most important factors. A sufficiently high molecular weight is necessary to prevent deformation of parts prior to cooling. HDPE is widely used for rotational moulding. The introduction of a crosslinking agent to form XPE is also possible.

The process is suitable for making small objects, normally with multicavity moulds, being in some cases unique. The thickness of parts is controlled by heat transfer and can be in the 3–6 mm (or 22 mm) range and uniform. Corners and edges are often thicker as a result of concentrated heat transfer. Certain shapes such as flat surfaces or thin ribs tend to be difficult to make, because of poor powder spreading or bridging. Moulded-in inserts (metallic or plastic) are easy to incorporate. Parts are largely free of residual internal stresses, but porosity problems often occur. The inner surface is relatively coarse (pucked, grained, orange skin), so the process is not applicable for precision parts. No scrap results from the process. Sequential moulding of successive distinct layers (lamination) is also possible, material being added in succession at suitable temperatures.

7.3.6 Compression Moulding

Compression moulding requires cooling of the mould after shaping a part and is not commercially attractive. Exceptions include the moulding of extremely viscous UHMWPE or special products.

7.3.7 Injection Moulding

The construction of injection moulds requires materials with a combination of good heat conductivity and resistance to mechanical wear and abrasion (low-melting alloys). Attention must be paid to shrinkage during cooling. Cavities are cut somewhat larger than the desired product, with typical linear shrinkage allowances between 0.2 and 5% for amorphous and highly crystalline thermoplastics, respectively. Since fast flow rates are needed, grades with high fluidity (high melt index) are normally preferable. The major advantage of injection-moulded products is the possibility of incorporating fine details such as bosses, located pins, mounting holes, and flanges, which can eliminate the need for assembly and finishing operations. Problems are concerned with shrinkage, warpage, sink marks, flashing, and short shots.

Melt temperatures for HDPE should be 200–300 °C with mould temperatures of 10–80 °C. A high mould temperature will improve the brilliance and appearance of a part. Mould shrinkage lies between 1.5 and 3%, depending on processing conditions, rheology of the polymer, and thickness of the final piece. Melt temperatures for LDPE injection moulding are 160–260 °C. Mould shrinkage lies between 1.5 and 3.5%. Injection moulding of LLDPE takes place at melt temperatures of 160–260 °C. For PE with 30% glass fibres, melt temperatures of 210–300 °C and mould temperatures of 5–70 °C are recommended.

7.4 Product Design

For products having a basically uniform cross-section, techniques involving continuous manufacture include the following: extrusion, extrusion covering, film blowing; techniques involving the shaping of a deformable polymer preform against a mould surface, which include sheet thermoforming and blow moulding; techniques involving gradual build-up of a polymer layer against a mould surface, which include coating and rotational moulding; and techniques involving the complete filling of a mould cavity, which include casting, compression moulding, and injection moulding.

Design for simultaneous rigidity and toughness is very difficult because these are opposing material properties. Occasionally in some applications both high rigidity and toughness are required. In these cases relatively thick sections are necessary. Selection of the appropriate grade is the first step. Filled and reinforced grades (mainly stiffened locally using metal or other reinforcing material) offer high rigidity at the expense of impact strength. The increase in thickness as a method to obtain an improvement of the rigidity and impact strength leads to an increase of the weight and slower

cooling of the product in the mould. Ribs are effective with minimum increase in the weight, but incorporation of ribs has the disadvantages of higher tool cost and reduction of impact strength due to concentration of stress and sink marks. To avoid stress concentration a curvature can be provided in the design or stepped sections can be incorporated if the problems with design of cooling channels in the mould are solved. Impact strength can be improved by providing thick sections where the structure is rigid by shape and construction, or a mechanism of deflection in less rigid structures according to the direction of impact.

The strength of a material at a weld line can be less than 50% of the reported overall strength of the material. Reinforced PE is more affected by the weld line problem because the reinforcement does not bridge the weld. The design of the mould and product plays a crucial role, although the weld strength can be controlled using high temperatures and pressures. The weakest weld appears where two flow fronts meet at 180°. Improvements can be made by the merging of two flow fronts, using knock-out holes and flow leaders.

Mould shrinkage depends on the processing conditions: very fine dimensional tolerance in PE is difficult to obtain. If a moulding deforms under small load or no-load conditions, the cause is usually post-moulding differential shrinkage, which often results in warpage or internal stresses. This problem can be visible as soon as the part is ejected from the mould or after a longer time depending on the temperature and load during service.

A constant wall thickness is required to avoid the entrapment of air during moulding and to avoid warpage resulting from differential cooling and shrinkage. Thin sections cool more rapidly than thick ones and consequently shrinkage in the former will be greater. In the case of box-shaped mouldings the situation is different, because deformation can occur even if the thickness is uniform. The straight sidewalls tend to bow inwards. External ribs or a tapered wall thickness can stiffen the moulding preventing distortion.

To create the right dimensions in a moulded part, the dimensions of the mould cavity must be increased by an amount known as the shrinkage allowance. Shrinkage will be greater in the direction of the flow than in the transverse direction mainly because of long polymer chains that undergo partial orientation by stretching during melt flow. Differential shrinkage results in distorted or warped mouldings. It is more important in materials with a broad MWD than in those with a narrow MWD. Where close tolerances are necessary, the differential shrinkage must be taken into consideration in the design process.

The injection pressure in a mould cavity decreases with distance from the gate, gate location and shape, and number of gates. Hence for complex mouldings there will be large differences in the shrinkage. Post-mould shrinkage accounts for about 1% for unfilled material and 0.5% for filled and reinforced grades. It is observed for 24 hours after moulding and will continue after this period but at a slower rate. Post-mould shrinkage is time and temperature dependent.

PE sink marks and voids appear in areas where sudden changes in section thickness occur or over ribs and bosses. Voids appear mainly when the external skin is rapidly cooled and becomes rigid. Sinking or surface depression occurs in localised thick sections where internal mass contains sufficient heat to keep the polymer in the melt state, so that it crystallises slowly producing sink marks. Reducing the effects of sink marks and voids can be achieved by maintaining the wall thickness, camouflaging the sink marks in the design, or placing beads or decorations on possible locations of sink marks.

7.5 Assembly

PE is prone to creep, and screws used under high stress for assembly may slacken due to creep. Metal inserts and treads can be used to increase the load-bearing area. They may be moulded in

or pressed in after injection moulding. Stress concentration effects on the impact strength due to sharp edged inserts should be carefully considered.

External and internal undercuts for snap-fit assembly parts should be also taken into consideration in design. External undercuts are demoulded using retracting segments of the mould while for internal undercuts the wall of the mould should be free to flex outwards during injection.

It is well known that the properties of plastics are dependent on time, temperature, and stress, so failure of products can occur months or years after design, manufacture, and testing. Hence a proper assessment of durability is necessary. PE components are designed as structures even at small loads and deformations because their stiffness and strength are orders of magnitude less than those of conventional materials (metals or other construction materials). The deformation of a component over a given period of time should not exceed 0.25% for a given stress. Viscoelastic behaviour must be taken into account in mould design. Long-term creep and fatigue data should be used to ascertain the long-term durability of PE products. To avoid catastrophic failure due to tertiary creep, the durability of products should be checked using elevated-temperature testing. Short-term standard testing must be considered only as a guide, and properties must be measured under service conditions.

The property values determined from long-term (strength) tests must be divided by a safety factor. The recommended safety factor for maximum permissible deformation is 1.2 while for calculations of safety as regards fracture, factors of 1.3–5 are advised depending on the stress and risk to property and persons. The long-term recommended design stress might be 6–10 times lower than the short-term yield strength. The safety factor in the design of reinforced materials is high in comparison to unreinforced materials. Safety factors of 2–3 for fracture and 1-2 for changes in dimension are recommended.

7.6 Mould Design

The flow ratio depends on MFR, processing conditions, and mould features. It is directly proportional to mould thickness, melt temperature, and injection pressure. Its values are important to establish the number and position of feed points.

The flow properties of a material can also be investigated using a spiral flow test. The melt is injected into a spiral mould cavity. The melt will freeze at a certain distance along the spiral channel (spiral flow length) depending on the flow properties and cross-sectional thickness of the spiral. The raw material manufacturer usually gives these values as material specifications.

A feed system to a mould has three main components: sprue, runner, and gate. Runner layouts are designed for plastic melts to deliver the melt at the same time and at the same temperature, pressure, and velocity to each cavity of a multicavity mould. In a balanced runner all cavities fill at the same time at the same pressure. Usually, this consumes more material than an unbalanced type but this disadvantage is outweighed by the improvement in the uniformity and quality of mouldings. Unbalanced mould runners cause overpacking, warpage, differential shrinkage, brittleness, dimensional inconsistency, and adhesion of parts to the mould. General recommendations for the design of gates are that they should be placed near thick sections for complete filling, they should be easily removable, they must assure symmetry in flow and avoid gas traps and weld lines, they should not be placed in parts that are subjected to high stresses, and they should minimise differential shrinkage.

Venting is necessary to avoid a short shot or burning of material and also to allow easy and quick mould filling at a lower injection pressure. In some cases the location of vents is quite obvious, while in complex cases mould flow simulation packages can predict the location of vents before machining the mould. Thin-walled mouldings require high injection speeds. In such cases the location of the vents is important.

Cooling channel design is very important, particularly for HDPE due to the higher heat capacity, to achieve a good quality moulding in a minimum time cycle. The cooling time depends on the wall thickness, melt temperature, mould temperature, resin stiffness, and rate of crystallisation. If the wall thickness is doubled, the cooling time is increased by 3–4 times. High mould temperatures are sometimes desirable to avoid distortion and to encourage flow over long distances. Surface gloss is improved by the use of high mould temperatures and voids may be eliminated, but any sinking may be accentuated. The size of a moulding is controlled to a small extent by the mould temperature. The shrinkage increases as the rate of cooling decreases, although very fast cooling has undesirable effects on the physical properties and surface appearance of products. The design of the cooling process must take into account that the whole moulding should cool to the ejection temperature at the same time.

The proper design of a taper will ensure easy ejection of a product from a mould – see previously.

Ejectors leave witness marks on mouldings, and hence it is preferable that they operate on sidewalls, ribs, or bosses. They should have sufficient diameters. A stripper plate acts on the entire wall of a part and so distributes the ejection force. Cylindrical ejector pins are most commonly used, although in constricted areas rectangular pins or blade ejectors can be used. For thin-walled articles, air-assisted ejection can be used.

Electrodeposition, casting, photoetching, and spark erosion are used to provide textured mould surfaces. The faithful reproduction of a textured surface is obtained with a low resin viscosity and good elasticity to permit the withdrawal of the textured surface. The role of the taper will be increased in these cases, as well as the gating system, since merging flow fronts can cause surface defects on the moulded product.

Besides the requirements for unfilled grades, for filled and reinforced grades the following considerations are necessary. Abrupt changes in cross-section should be avoided to reduce the degradation of the reinforcing fibres; melt accumulation and degradation should be avoided, because filled grades are more temperature sensitive than unfilled grades; notches (transitions, corners, edges) should be avoided using a rounding-off radius of greater than 0.5 mm; greater draft for ejection should be provided, for example, 0.5–1°; and the orientation of fibres should be carefully considered to improve weld-line strength.

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8 Post-Processing and Assembly

Post-processing and assembly methods are the operations that determine the final nature of end products. Moulded polyethylene (PE) articles may be subjected to several operations such as joining by welding (friction, vibration, hot gas and hot plate, ultrasonic, radio frequency) or gluing, machining, or decorating (Table 8.1) [1].

Table 8.1 shows that PE is difficult to bond, paint, and plate; high-density PE (HDPE) is easy to machine while low-density PE (LDPE) is not. Suitable welding techniques for both types of PE are friction, vibration, hot gas, and hot plate welding. Ultrasonic welding is difficult, especially for LDPE, while radio frequency welding is impossible for both types.

Table 8.1 Comparison of post-processing properties of PE and other competing materials. On a scale of 0 to 9, where 0 represents an unfavourable property and 9 represents a favourable property						
Property	LDPE	HDPE	PP	HIPS	PVC	ABS
Bonding	5	5	5	9	9	8
Machining	5	8	8	4	5	9
Painting	1	4	4	8	6	8
Plating	0	0	0	1	0	6
Friction welding	8	8	9	8	8	8
Vibration welding	8	8	9	8	8	8
Hot gas welding	7	7	9	7	9	6
Hot plate welding	8	8	9	8	9	8
Ultrasonic welding	2	5	4	7	5	9
Radio frequency welding	0	0	0	0	8	0
<i>ABS: acrylonitrile-butadiene-styrene</i>			<i>HDPE: high-density PE</i>			
<i>HIPS: high-impact polystyrene</i>			<i>LDPE: low-density PE</i>			
<i>PP: polypropylene</i>			<i>PVC: polyvinyl chloride</i>			

8.1 Joining

Almost without exception, the joining of PE parts is carried out by any of the various heat-seal techniques. This type of joining is one of the major benefits of PE pipe. However, in some cases stab-type mechanical fittings can be used to provide a leak-free union between pipe ends that is stronger than the pipe itself. Due to crosslinking effects, crosslinked PE (XPE) can be joined by mechanical couplings that are not typically used on non-XPE pipe because of creep, cold flow, and stress cracking concerns. There are several types of mechanical coupling systems available for XPE tubing, such as compression, flare, and crimp ring. Since mechanical connections must be accessible, fusion joints are typically used wherever possible. Butt, socket, or electrofusion techniques are used to join individual sections of pipe. ‘U’-bend fusion fittings are used for creating the return line in vertical bores. In fact, it is common for PE pipe made for geothermal heat exchangers to be double wrapped on a coil and the ‘U’-bend fitting fused on at the point of manufacture. Sidewall fusion can be used to join parallel pipe loops to a header. All fittings must be pressure rated for the expected operating and surge pressures, and joined according to the manufacturers’ recommended procedures. Repairing a leaking joint could be very difficult. However, due to the fact that very strong fusion joints can be made with PE pipe, this concern is easily overcome.

Surface treatments tend to increase the maximum temperature at which heat sealing can be carried out. For sealing films, bar sealers, impulse sealers, band sealers, hot wire sealing, glow bar sealers, flame sealing, heated roller sealing, and hot melt sealing can be used. Moderately strong joints can be obtained using epoxy resins or other high-strength adhesives when applied to a treated PE

surface. For the sealing of heavy PE sections, hot gas welding, friction or spin welding, hot plate welding, embedded resistance wire welding, or cold heading are used.

8.1.1 Welding

The choice of welding technique depends on the area of the joint and the number and shape of the parts to be joined. The strength of the welding depends on the geometry of the component, welding method, and welding parameters (temperature of the hot plate, heating time, welding pressure, and welding time).

8.1.1.1 Heated Tool Welding

In heated tool welding, a heated plate is used to melt the joining surfaces of two thermoplastic parts. The interfaces in contact cool together providing a hermetic seal. The main characteristics are hot plate, socket, butt, and saddle. If the correct procedure is used, the weld strength may be equal to the tensile strength of the parent material. Weld times range from 10 seconds for small components to 60 minutes for large-area components.

For welding HDPE pipes, socket welding is used where a heated pipe is inserted into a heated fitting. Electrofusion fittings are used in exceptional circumstances where socket welding is not possible. Socket welding is preferred for joining HDPE pipes for domestic installations while heated butt fusion is the most common method of joining HDPE pipes for industrial installations. The cut surfaces of the pipes are planed, heated in contact with a heated element, and then joined and cooled under pressure. Valves and other armatures can be incorporated by flanging, welding, or threading.

8.1.1.2 Hot Gas Welding

This method uses a stream of hot gas (air) directed towards the joint between the two thermoplastic parts to be joined, where it softens or melts the polymer. There are variations in technique, including hand welding, speed welding, and extrusion welding. A thermoplastic filler rod can be used to form a weld. Hot gas welding is a manual process and the quality of the bond depends on the skill of the operator. The adjustable parameters are gas type, flow rate, temperature, and the angle of the filler rod of the parts being welded.

8.1.1.3 Friction and Vibration Welding

In friction welding, heat is generated by pressing one of the parts to be joined against the other and rapidly vibrating it. Variations are linear vibration welding, orbital friction welding (circular movement), spin welding, and angular friction welding. The main parameters are rotational speed, friction pressure, displacement, and duration. The duration is about 2–3 seconds. Further time is required to align the parts and to hold them together under pressure until a solid bond is formed. Both filled and unfilled PE can be assembled using linear and angular friction welding. The welding capacity is proportional to the coefficient of friction of the plastic material. The modulus of rigidity does not influence the welding process. Using friction welding two different materials can be joined, such as PE and polyamide. Rotational friction welding relies on the friction produced by rotating and pressing one part against another until the fusion temperature is reached. The parameters influencing weld quality are rotational speed, friction pressure, friction time, and applied pressure time (Table 8.2).

8.1.1.4 Ultrasonic Welding

High-frequency (20–40 kHz) sound energy is used to soften or melt the thermoplastic at a joint. This technique is very fast and can be easily automated. The welds are strong, clean, and reliable. PE do

Table 8.2 Rotational friction welding parameters for high-density PE pipes

Pipe diameter (mm)	Difference between outside and inside diameter of pipe (mm)	Quality coefficient of friction welding	Rotational speed (rpm)	Friction time (s)	Time of application of pressure (s)	Total time (s)
50	1.5	1	500–1000	10–20	20	40–80
100	2.5	1	200–400	20–30	10	60–120
150	3.0	1	100–250	30–40	10	80–140

not transmit ultrasonic waves well enough to enable them to undergo far-field ultrasonic welding. The presence of titanium dioxide and butadiene reduces the efficiency of ultrasonic welding. The advantages of this method are that there is no toxicity, it is non-flammable, and there is no waste associated with high productivity.

8.1.1.5 Other Welding Techniques

Other welding techniques include laser welding, infrared welding, electromagnetic welding (recommended for PE pipe and PE pipe system joints), and microwave welding in which radiation is used to increase the temperature, but they are established only for a limited number of cases. Infrared welding is applied for LDPE, HDPE, and PP films, foils, sheets, and parts having thickness ranging from 0.05 to 2 mm.

Solvent bonding is not possible because of the high resistance of PE to solvents.

8.1.2 Adhesive Gluing

Adhesive gluing for joining parts is applied after an adequate treatment of the surfaces by flaming, corona discharge, and primer [similar to the treatments used for decorating and printing (see Section 8.3)]. The adhesives for bonding PE are contact adhesives based on polyurethanes or synthetic rubber, two-pack adhesives based on epoxy resins, polyurethanes, phenolic resins, and others, ethylene–vinyl acetate hot melt adhesives, pressure-sensitive adhesives, and polyurethane contact cements. The factors affecting the choice of adhesive are resistance to chemicals, moisture, high temperature, and vibrations. The strength of a joint depends on its geometry and the adhesive used.

8.1.3 Sealability

Sealability is very important in film packaging applications. Copolymers offer improved sealability compared to homopolymers.

8.2 Assembly and Fabrication

8.2.1 Machining

PE, being a soft material, is easy to machine using carbide-tipped or high-speed steel tools on conventional metalworking or woodworking machines. High cutting speeds or low feed rates are required for optimal finishes. Sawing, turning, milling, planing, threading, routing, chiselling, and drilling can be applied using sharp tools. The heat generated can be dissipated using cooling water or emulsions.

8.2.2 Snap-Fit Joints

In a snap-fit fastening, two parts are joined through an interlocking configuration that is moulded into the parts. A protrusion on one part is briefly deflected during joining to catch in a depression or undercut moulded into the other part. This technique is used in the assembly of tools, housings, electronic components, medical devices, and others. The joints are designed to be stress free during use to prevent creep and stress relaxation. The joints are either easily released or permanent depending on the locking angle. Snap-fit joints require more attention to the engineering design and can fail during assembly or use if not designed properly.

8.2.3 Mechanical Fastening

Mechanical fasteners are screws and bolts, self-tapping screws, or inserts. They may be reusable and can be moulded in metal or plastic. Plastic fasteners are of low weight and are corrosion and impact resistant. The high stress produced near fasteners can make parts more susceptible to chemical and thermal attack. The design stress, residual stress, and assembly stress in a component should not exceed the maximum allowable stress for the plastic. To reduce the stress concentration, inserts with smooth rounded surfaces can be used, which produce less stress than knurled inserts.

8.3 Decorating

In pressure embossing, the design is engraved on a steel roller, which is water-cooled on the inside. The PE film to be embossed is preheated and fed between the engraved roller and a rubber roller.

Decoration may be realised by coating (printing, painting, metallising, and electroplating), by an appliqué (surface covering or adhesive film), or by impression (hot stamping). Painting is applied to provide colour, finish, or cover imperfections. Paints and coatings can provide enhanced properties such as improved chemical, abrasion, and weathering resistance and electrical conductivity.

Surface pre-treatment by the methods mentioned in Section 8.1.2 can be applied. Chemical pre-treatment by dipping in a chromosulfuric acid bath is also possible as is UV irradiation, mainly for parts with complicated shapes. Coating generally leads to a reduction in the impact strength.

8.3.1 Printing and Painting

Printing processes suitable for PE are pad transfer, screen printing, laser printing, dyeing, and fill and wipe. In valley printing, an additional ink-furnishing roller is used to ink the highest spots on the embossing roller. In vacuum embossing, the roller is engraved in the reverse manner; fine holes in the deepest part of the pattern through to the inside of the roller permit the application of suction. Due to the non-polar nature of PE, the choice of primer or surface treatment is very crucial for printability and paintability.

8.3.2 Metallising and Electroplating

In vacuum metallising, a metal is heated in a vacuum chamber to its vapourisation point, which is lower than the melt temperature of plastics. The metal vapour deposits on the cooler plastic surface. In electroplating, an electric current is used to deposit metal from a metal salt solution onto a plastic rendered conductive by electroless plating. Arc flame, arc spraying, and sputtering are other techniques used. Metallising requires very clean surfaces, free from mould release agents. Primers or pre-cleaners can be used to improve the adhesion of the metal to the polymer surface.

8.3.3 Appliqués

Appliqués or surface coverings can be applied using heat or pressure. The methods used include hot stamping, decals, hot transfer, water transfer, and in-mould decorating. Decals are decorations or labels printed on carriers such as paper or plastic with pressure-sensitive adhesives. The adhesive backing must be compatible with PE and should not cause cracking or crazing. Clean surfaces, free of mould release agents and with minimal sink marks and projections are also requirements for good decoration.

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Abbreviations

HDDMA	1,6-Hexanediol dimethacrylate
ABS	Acrylonitrile-butadiene-styrene
AL	Aluminium
ASTM	American Society for Testing and Materials
PI2	An isomeric mixture of alkyl-substituted benzophenones
aPP	Atactic PP
ATRP	Atom transfer radical polymerisation
AIBN	Azo butyronitrile
BOPP	Biaxially oriented PP
BUR	Blow-up ratio
BHT	Butylated hydroxytoluene
CPE	Chlorinated Polyethylene
CRT	Clean reactor technology
XPE	Crosslinked polyethylene
Cp	Cyclolefins
DIN	Deutsches Institut für Normung eV
DEBADM	Diethoxybisphenol A dimethacrylate
DSC	Differential scanning calorimetry
DDR	Drawdown ratio(s)
DMTA	Dynamic thermal analysis
ESCR	Environmental stress crack resistance
EPDM	Ethylene propylene diene terpolymer
EBA	Ethylene-butyl acrylate
EMA	Ethylene-methacrylic acid
EP	Ethylene-propylene
EVA	Ethylene-vinyl acetate copolymers
EVOH	Ethylene-vinyl alcohol
EPE	Expandable PE
FCC	Fluid-bed catalytic cracking
GP	General purpose
T _g	Glass transition temperature(s)
mHDPE	HDPE produced using metallocene catalysts
HDT	Heat deflection temperature
HDPE	High density PE (s)

HLMFR	High load melt flow rate
HMW	High molecular weight
HMWHDPE	High molecular weight HDPE
HMWPE	High molecular weight PE
HAO	Higher alpha-olefin
HIPS	High-impact polystyrene
HALS	Hindered amine light stabiliser
HAS	Hindered amine stabilisers
HB	Horizontal burn
HIC	Hydrogen-induced cracking
NOH	Hydroxylamine
ICI	Imperial Chemical Industries
IR	Infra red
iPP	Isotactic PP
L/D	Length to diameter ratio
LS	Light scattering
LOI	Limiting oxygen index
LLDPE	Linear low density PE(s)
mLLDPE	LLDPE produced using metallocene catalysts
LCB	Long-chain branching
LDPE	Low density PE
LMWPE	Low molecular weight PE
LMDPE	Low-medium density PE
MMW	Medium molecular weight
MDPE	Medium-density PE
MFI	Melt flow index
MFR	Melt flow rate
T _m	Melting temperature
mC	Metallocene catalyst
MA	Methacrylic acid
MMT	Million metric tonnes
MMD	Molar mass distribution
MWD	Molecular weight distribution(s)
NOR-HALS	N-alkoxy HALS
NMWD	Narrow molecular weight distribution
NSF	National Science Foundation
M _n	Number average molecular weight

MO	Osmometry
mPE	PE produced using metallocene catalysts
POP	PO plastomer(s)
PB	Poly-1,4-butadiene
PA	Polyamide(s)
PA6	Polyamide 6
PA6.6	Polyamide 6.6
PDMS	Polydimethylsiloxane
PET	Polyethylene terephthalate
PETG	Polyethylene terephthalate glycol
PE	Polyethylene(s)
PO	Polyolefin(s)
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
RM	Reference material
RH	Relative humidity
RAFT	Reversible addition-fragmentation chain transfer
rpm	Revolutions per minute
SCORIM	Shear-controlled orientation in injection moulding
SSC	Single-site catalyst(s)
SEC	Size exclusion chromatography
SRM	Standard reference material(s)
TREF	Temperature rising elution fractionation
TDPA	Totally degradable plastic additive
TAIC	Triallylisocyanurate
UHF	Ultra high frequency
ULDPE	Ultra low-density PE
UHMWPE	Ultra-high molecular weight PE
UV	Ultraviolet
UVB	Ultraviolet B radiation
UL	Underwriters Laboratories Inc.
USDA	US Department of Agriculture

FDA	US Food and Drug Administration
NIST	US National Institute of Standards and Technology
VLDPE	Very low-density PE
VA	Vinyl acetate
M_w	Weight average molecular weight
WLF	Williams-Landel-Ferry
ZN	Ziegler-Natta

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