



Qenos

01

GENERAL PROPERTIES

—
TECHNICAL GUIDE



Alkathene® Alkatuff® Alkamax® Alkadyne® Alkatane®



Front Cover

Tensile testing reveals much about the mechanical properties of polyethylene products. Qenos manufactures and tests product samples in accordance with standards such as ASTM D638 and ASTM D882. Data collected includes tensile stress and tensile modulus, elongation at break as well as yield stress and strain. The resulting stress/strain curves are used by Qenos for product integrity, specification development and product and process improvement purposes.

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GENERAL PROPERTIES

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1 GENERAL PROPERTIES

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INTRODUCTION

Polyethylene is a versatile thermoplastic polymer consisting of long hydrocarbon chains. It is chemically synthesised from ethylene, a compound that is usually derived from petroleum or natural gas. Polyethylene polymers can be broadly categorised into branched and linear polyethylenes, however, categorisation is more commonly based on polymer density. The physical properties of the polymer depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. LDPE, LLDPE, mLLDPE and HDPE grades are the most common types of polyethylene.

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WHAT IS POLYETHYLENE?

Polyethylene or polythene, as it is also known, is a polymer produced by the polymerisation of ethylene gas, a derivative of the petroleum industry. The polymer consists essentially of long-chain molecules of very high molecular weight, made up of many thousands of the -CH₂- repeating unit (see Figure 1).

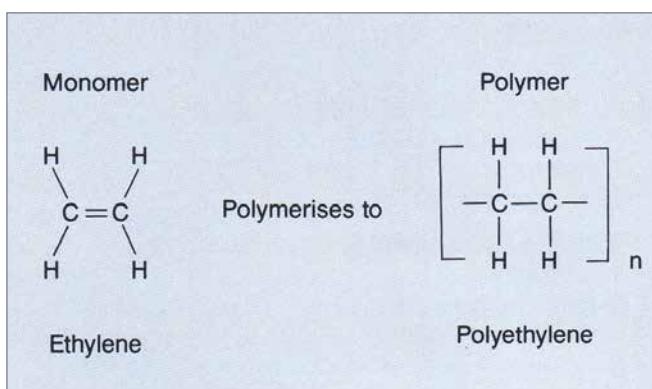


Figure 1: Polymerisation of Ethylene to Polyethylene

Ethylene can be polymerised to produce polymers of any desired molecular weight, from oils, greases and soft waxes at low molecular weights to tough flexible polymers, the polyethylenes, at high molecular weights.

Types of Polyethylene

Depending on the polymerisation process used to produce the polyethylene (see later), the polymer can be a linear molecule or it can be highly branched. The degree of branching affects how the molecules pack together, i.e. the density of the polymer. Polyethylenes can range in density from about 0.900 g/cm³ to 0.970 g/cm³.

There are several basic types of polyethylene, classified by means of the density of the polymer:

- **Low Density Polyethylene (LDPE)** refers to polymer with a density between 0.915 and 0.930 g/cm³.
- **Linear Low Density Polyethylene (LLDPE)** refers to low density type polymer with a density between about 0.915 and 0.940 g/cm³, made via an HDPE type manufacturing process.
- **Metallocene Linear Low Density Polyethylene (mLLDPE)** refers to tougher LLDPE type polymer with a density between about 0.915 and 0.940 g/cm³, made using metallocene catalysts.

- **Medium Density Polyethylene (MDPE)** refers to polymer with a density between 0.930 and 0.940 g/cm³.
- **High Density Polyethylene (HDPE)** refers to polymer with a density between 0.940 and 0.970 g/cm³.

MANUFACTURE OF THE VARIOUS TYPES OF POLYETHYLENE

The various types of polyethylene are made by different processes. These processes are described in Appendix 1, and are summarised below.

LDPE is produced by high pressure free-radical polymerisation of ethylene, with pressures up to 200 MPa and temperatures up to 300°C. The polymer is highly branched, with both short and long chain branches. This process is used by Qenos to produce the *Alkathene* range of LDPE. Such LDPE is sometimes called branched polyethylene or high pressure polyethylene.

HDPE is produced at low pressures by slurry, or gas-phase processes using Ziegler-Natta transition metal catalysts. These processes are used by Qenos to produce the *Alkatane* and *Alkadyne* range of HDPE. The polymer is basically linear, with little or no branching, depending on whether comonomer was used during the polymerisation process.

mLLDPE is also produced by the low pressure polymerisation technology using metallocene catalyst to copolymerise ethylene and another monomer such as butene-1, or hexene-1. This process is used by Qenos to produce the *Alkamax* range of mLLDPE. The metallocene catalyst produces resins with very consistent and specific properties such as superior toughness and stiffness balance.

MDPE and LLDPE products are produced by the low pressure polymerisation technology using transition-metal catalysts, however, comonomers are introduced into the reaction to create small short chain branches on the linear molecule, with the effect of reducing the density. This process is used by Qenos to produce the *Alkatuff* range of LLDPE. Qenos produces these products in Australia using the gas-phase polymerisation process, with hexene-1 as the comonomer.

STRUCTURAL DIFFERENCES BETWEEN THE POLYETHYLENES

The variations in chemistry between the processes produce important differences in the structure, and consequently the final properties, of the various polyethylenes. The different branching structures for LDPE, LLDPE and HDPE are illustrated in Figure 2.

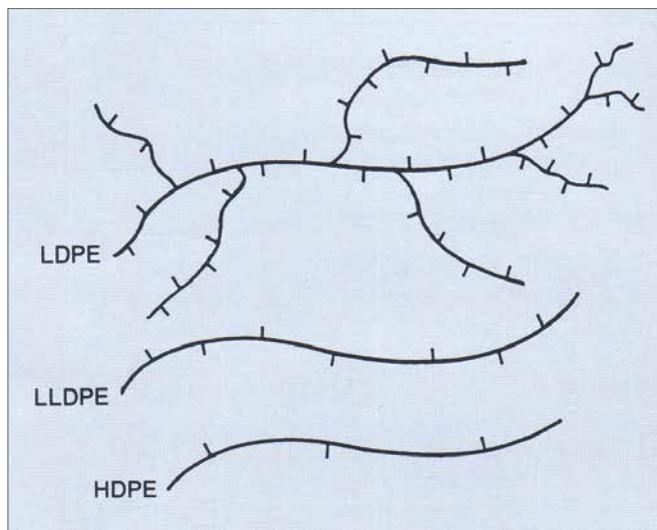


Figure 2: Schematic Representation of Different Branching Structures in Polyethylene

LDPE made by the high pressure route is characterised by a significant level of long chain branching (typical branch length of several hundred carbon atoms, long chain branching frequency up to 5 per 1,000 carbon atoms), as well as short chain branching (2 to 6 carbon atoms long).

HDPE is essentially a linear molecule with a very low level of short chain branching.

LLDPE is again a linear molecule with a higher level of short chain branching than HDPE (specifically introduced by polymerisation with comonomer), but without the long chain branches which characterise LDPE.

MDPE and mLLDPE resemble LLDPE in structure.

The specific effects of these differences in branching on the crystallinity, rheology and mechanical properties of the polymers will be highlighted in the following text.

HISTORY OF POLYETHYLENE

ICI Discovers Polyethylene

Polyethylene was first discovered in 1933 at ICI's research laboratory at Winnington in England, as a result of experiments on ethylene gas at very high pressures. By chance, the scientists, Fawcett and Gibson, found a white waxy powder in the reactor and this proved to be a polymer of ethylene, today known as low density polythene or LDPE.

By the late 1930s, developments had progressed and in 1938 a large potential market was recognized to replace gutta-percha for submarine cable insulation, because of the polymer's remarkable electrical properties. As a result of initial successful trials, a full-scale polyethylene plant with a capacity of 100 tons came on stream in 1939.

Almost the entire production of polyethylene during World War II was used for the insulation of high frequency radar cables. Union Carbide Corporation and Du Pont commenced full-scale production in the United States in 1943. By 1955 there were 13 producers worldwide and total output was about 200,000 tons; development accelerated as processing by film extrusion and injection moulding was established and new applications were found.

Low Pressure High Density Polyethylene

In 1953, it was discovered that ethylene could be polymerised at low pressures to form a linear polymer with high crystallinity and density. This new polyethylene was high density polyethylene (HDPE) and it resulted from the work of Ziegler on the low pressure polymerisation of ethylene using organo-metallic catalysts. This process was commercialised by Hoechst AG in Germany in 1955. Other processes using different catalysts were developed by Phillips Petroleum Co. and Standard Oil of Indiana.

Since the early work of Ziegler, many improvements in catalyst types and efficiencies have occurred. In 1972, Union Carbide Corporation introduced their fluidised-bed gas-phase process for producing HDPE, whereas the earlier processes were carried out in solution or slurry.

Linear Low Density Polyethylene

The challenge for the scientists was to make LDPE by the low pressure organo-metallic catalyst route. In the early 1960s, Du Pont of Canada successfully developed their "Sclair" range of polyethylenes made by a low pressure solution process, but they only marketed the resins in specialty market areas.

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In 1977, Union Carbide Corporation announced that they could produce a low density polyethylene by their low pressure gas-phase process, with considerable cost savings over the original high pressure process. This polymer was a copolymer of ethylene with a small amount of propylene and had a linear structure with greater toughness than traditional low density polyethylene; it has since been called linear low density polyethylene (LLDPE). Later Dow Chemical introduced their "Dowlex" LLDPE, which was produced by a different (solution) process using octene-1 as the comonomer.

Subsequently, other comonomers such as butene-1, hexene-1, octene-1, and 4-methyl-pentene-1 have been used in place of propylene by various manufacturers using several different process technologies to produce a wide range of different LLDPEs. Ultra low density polyethylene and very low density polyethylene with densities at the bottom end of the spectrum have been introduced in recent years.

Each process and each comonomer leads to slightly different polymer structures. For example, Figure 3 shows how the toughness of LLDPE improves as the comonomer type is changed (and hence the short chain branch length increased).

Metallocene Linear Low Density Polyethylene

In the early 1990s, Exxon Chemical Company, now ExxonMobil Chemical Company, developed revolutionary single-site metallocene catalysts for use in these UNIPOL™ gas-phase PE Process. Metallocene catalysts have enabled better control over the structure of the polyethylene molecule to achieve tailored performance and improved properties.

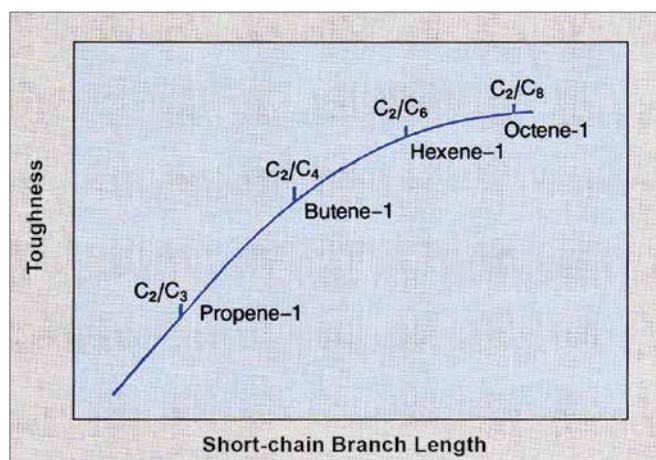


Figure 3: Effect of Comonomer Type and Short Chain Branch Length on Toughness Properties of LLDPE

FORMS OF LDPE

Alkathene LDPE is supplied in a number of different forms. All grades are available as pellets, either as virgin polymer (without any additives) or as formulated polymer (containing an antioxidant and, for some film grades, slip, antiblock or possibly antistatic additives).

The range of grades available for Alkathene can cover densities from 0.915 to 0.928 g/cm³ and melt flow indices from 0.2 to 70 g/10 min.

- Note for convenience, the term Melt Flow Index or MFI defined the melt flow of polymer extrudate in g/10 min when subjected to a load of 2.16 kg – otherwise referred to as MI₂.

FORMS OF mLLDPE AND LLDPE

mLLDPE and LLDPE are supplied in pellet form, containing a basic stabiliser package for protection during processing and end-use. Film grades may be formulated with slip, antiblock, and process aid additives, as well as a basic stabiliser package.

The range of grades available for Alkamax mLLDPE and Alkatuff LLDPE can cover densities from 0.915 up to 0.938 g/cm³ and melt flow indices from 1.0 to 20 g/10 min.

FORMS OF MDPE AND HDPE

MDPE and HDPE are supplied in pellet form, containing a basic stabiliser package for protection during processing and end-use. Some grades are formulated with additional additives that perform unique functions such as UV protection. Alkadyne HDF193B is supplied as a black compound formulated with a stabiliser package and carbon black for UV protection.

The range of grades available for MDPE and HDPE can cover densities from 0.940 to 0.965 g/cm³ and melt flow indices from 0.06 to 10 g/10 min.

THE NATURE OF POLYETHYLENE

Molecular Structure of Polyethylene

The properties of a given polyethylene depend primarily on four factors:

- Its molecular weight (or average length of molecular chains),
- Its molecular weight distribution (MWD) (or the distribution of different chain lengths),
- Its degree of long chain branching, and
- Its degree of short chain branching (i.e. the number, length and distribution of the short branches)

All of these factors can be controlled during the polymerisation process.

The polymer molecular weight determines the mechanical properties and the melt flow behaviour of the polyethylene. The molecular weight distribution and degree of long chain branching also affect the melt flow properties such as shear thinning behaviour and melt elasticity. The degree of short chain branching determines properties such as crystallinity, density and stiffness. Some properties depend on all four factors.

As it is difficult to measure these basic parameters directly, it is convenient to use Melt Flow Index (MFI) to represent the number average molecular weight, Density to represent the degree of short chain branching and Melt Flow Index Ratio (MFR) to represent the molecular weight distribution (see below for explanation of MFI & MFR). The product is made to a specified MFI and density and these are correlated with the other properties. The MFI and density can be varied independently by the appropriate choice of process conditions.

Branching

LDPE consists essentially of long chain molecules, with a -CH₂- repeating unit, a number average molecular weight between 10,000 and 50,000, and branch points at intervals of every 25 to 100 carbon atoms in the chain (10 to 40 methyl groups per 1,000 carbon atoms). Most of the branches are short, being mainly ethyl (C2), butyl (C4) or pentyl (C5). The frequency of each group depends on the polymerisation conditions. Roughly 2 to 10% of the branches (1 to 5 per 1,000 carbon atoms) are long chains containing several hundred carbon atoms and each of these long chains has both short and long chain branches at the same frequency as the main chain.

The branches of a polyethylene molecule are terminated by either methyl groups or olefinic unsaturation. Since the latter is present in a very small proportion, the methyl group content will largely determine the total number of branches.

The methyl content and the amount and type of unsaturation can be measured by infra-red spectroscopy and a typical infra-red scan of LDPE is given in Figure 4. The unsaturated olefinic groups consist of pendent vinylidene, pendent vinyl and vinylene, with the first predominating; the total unsaturation ranges between 0.4 and 2 double bonds per molecule.

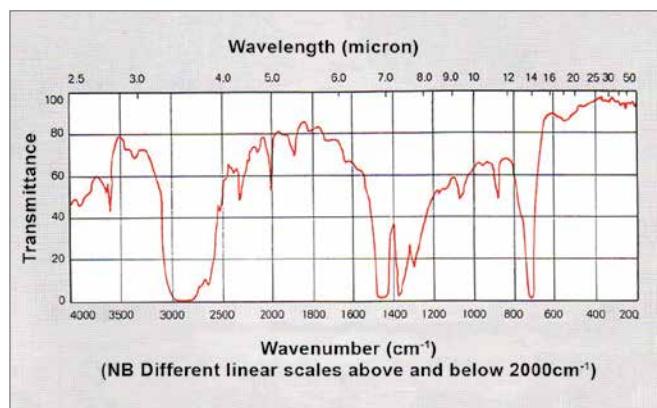


Figure 4: Typical Infra-red Spectrum for Low Density Polyethylene

In linear polyethylenes (mLLDPE, LLDPE, MDPE and some HDPE grades), the branching in the molecule is achieved through copolymerisation with comonomers such as butene-1, hexene-1 or octene-1. These comonomers respectively give ethyl (C2), butyl (C4) and hexyl (C6) branches. The degree of branching increases as the proportion of comonomer in the polymer is increased. The branching structure will hence depend on the type and proportion of comonomer, and also the distribution of comonomer along the molecule (i.e. whether the branches are evenly distributed or clumped together) and between molecules. This means that the linear polyethylene grades supplied by different manufacturers can have noticeably different properties. Figure 3 demonstrates how the toughness of different LLDPEs is highly dependent on the short chain branch length, i.e. the comonomer used.

In Alkatuff LLDPE, which is a hexene-1 copolymer, the branch points occur every 50 to 100 carbon atoms (10 to 20 methyl groups per 1,000 carbon atoms). As indicated earlier, there is no long chain branching.

Molecular Weight and Molecular Weight Distribution

Polyethylene consists of a mixture of molecules with a distribution of different molecular weights. The distribution of these molecular weights can be measured by means of Gel Permeation Chromatography (GPC) of dilute polyethylene solutions at elevated temperatures, and is characterised by the number and weight average molecular weights (M_n and M_w, respectively); the ratio M_w/M_n is a measure of the width of the molecular weight distribution (see Figure 5).

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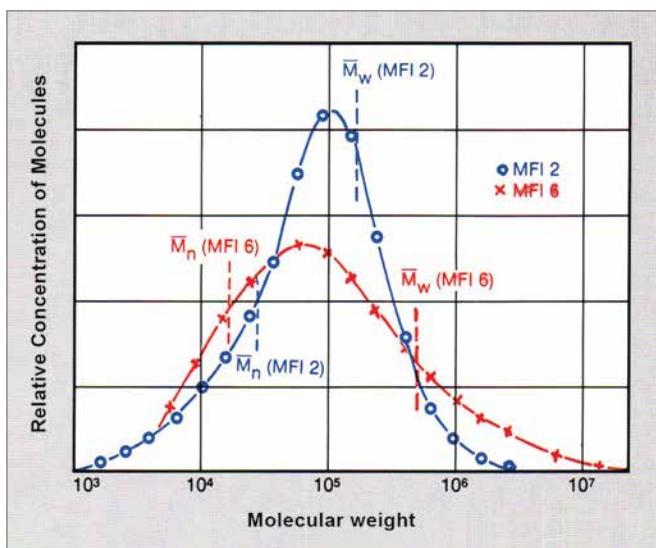


Figure 5: Typical Molecular Weight Distributions for Polyethylene, Showing Narrow (MFI 2) and Broad (MFI 6) Distributions

M_n = Number average molecular weight = $\sum(M_i N_i)/\sum N_i$

M_w = Weight average molecular weight = $\sum(M_i W_i)/\sum W_i$

where N_i is the number of polymer molecules of molecular weight M_i , and W_i is the weight of these molecules = $M_i N_i$.

The average molecular weight and the molecular weight distribution of polyethylene are governed by the polymerisation conditions. For LDPE, the reactor design also has an important effect and polymers made in a stirred vessel will have a different molecular structure to those made in a tubular reactor.

By varying the polymerisation conditions, it is possible to make products covering a wide range of molecular weights, molecular weight distributions and branching contents. Figure 5 illustrates the extremes of wide and narrow molecular weight distributions. For LDPE, polymers with a wide molecular weight distribution in general also have a high degree of long chain branching.

With linear polyethylenes, molecular weight distribution is basically controlled by the choice of the catalyst type.

LDPE grades generally have broad molecular weight distributions and the linear polyethylenes typically have narrower molecular weight distribution.

Crystallinity

The similarity in structure of the individual polyethylene molecules allows close packing of parts of the chain, giving a regular, ordered, three-dimensional network. However, because of the effects of chain entanglement and branching, restrictions are placed on the degree of ordering and this interferes with crystallisation. Polyethylenes are thus 'semi-crystalline' polymers, having a proportion of ordered, crystalline regions (often called crystallites) and also non-ordered 'amorphous' regions between these crystallites. LDPE will have smaller crystallites than LLDPE because of the different short chain branching structures. HDPE products can have even larger crystallites depending on the amount of comonomer that was used in the polymerisation process.

Polyethylene crystallises by a folded-chain mechanism to form a lamella-type structure similar to that depicted in Figure 6. Each lamella layer is about 100 carbon atoms thick. The branched parts of the molecule are excluded from the lamellae, either as folded loops or as 'tie-molecules' participating in adjacent lamellae. The longer side chains in hexene-based LLDPE compared with butene-based LLDPEs of the same density are believed to increase the number of inter-lamellar tie molecules, giving a reinforcing effect and resulting in a tougher product. This beneficial effect of increasing the short-chain branch length is shown in Figure 3.

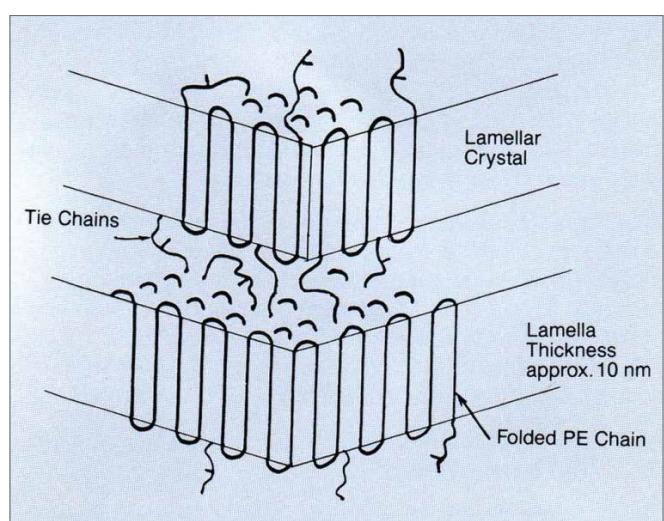


Figure 6: Schematic Representation of Polyethylene Lamella Structure showing Folded Chains and Tie Molecules

The lamellar crystallites grow in an approximately radial manner to form relatively large three-dimensionally ordered aggregates, known as spherulites. These spherulites can markedly affect the optical properties of a sheet of polyethylene as they act as light-scattering centres. They may be seen as a pattern of dark Maltese crosses when a thin sheet of polyethylene is viewed in a polarising microscope. Their size (which can be up to 100 microns in diameter) and distribution may also have an effect on the physical properties of the sample.

Typically, the higher the density of the polymer the higher the degree of crystallinity and the stiffer the solid polymer is. The overall size of the spherulites in the polymer crystals basically depends on the rate of cooling and branch length. When crystallisation occurs under stress, the lamellar and spherulitic structure is modified.

The proportion of crystalline material developed in any polyethylene sample is dependent firstly upon the structural features of the molecules (molecular weight, degree of branching, etc.), and also upon the conditions under which it is crystallised and any subsequent thermal treatment. Hence linear polyethylene will normally have a higher crystalline content than branched polyethylene crystallised under the same conditions, while fast cooling from the melt will normally yield lower crystallinities than slower cooling.

LDPE has crystallinity values in the range 40% to 65%, depending on the degree of branching and thermal history LLDPE may have similar crystallinities to LDPE. On the other hand, HDPE has much higher crystallinity, viz. 60 to 85%.

Density

There is a direct relationship between the density of the polyethylene and its crystallinity, as has been intimated in the previous discussion. As density is easier and more convenient to measure, it is usual to quote the density of a polyethylene rather than its crystallinity. The density of polyethylene can be measured by means of the density gradient method (ASTM D1505) or by the titration technique.

Density figures for the LDPE polymers range from 0.915 g/cm³ to 0.928 g/cm³ at 23°C. Density figures for the LLDPE polymers range from 0.915 g/cm³ to 0.938 g/cm³ at 23°C. Density figures for the HDPE polymers typically range from 0.940 g/cm³ to 0.970 g/cm³ at 23°C.

Behaviour on Heating

There is normally a wide variation in the size and perfection of the crystallites which form in a sample of polyethylene. During heating this results in a wide melting distribution which can commence at quite a low temperature. Examples of such distributions are shown by the Differential Scanning Calorimeter (DSC) heating scans in Figure 7. These scans show that while the melting point quoted for a polymer is generally the peak temperature, a considerable proportion of crystalline polymer has already been melted at much lower temperatures.

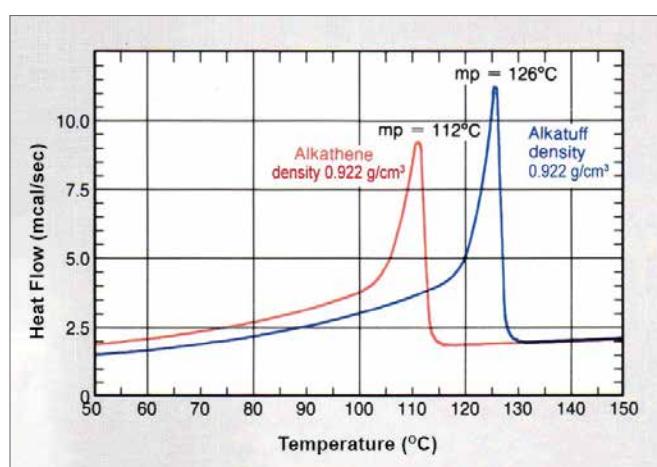


Figure 7: DSC Heating Curves for Alkathene LDPE and Alkatuff LLDPE of Density 0.922 g/cm³ (Heating Rate 20°C/min)

Typical values of the peak melting temperature and enthalpy for different types of polyethylene are shown in Table 1 below:

Table 1: Polyethylene – Peak Melting, Crystallisation Temperatures and Enthalpy of Melting

Resin Type	Peak melting Temperature °C	Enthalpy of Melting (J/g)	Major Crystallisation Temperature °C
LDPE	112	103	95
LLDPE	126	160	107
HDPE	134	203	118

The perfection of the crystallites and the overall crystallinity are mainly influenced by the degree and distribution of branching in the molecule. The temperature at which the crystallites melt depends primarily on this branching. Thus a highly crystalline polymer, with a low degree of branching, will melt within a higher temperature range.

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Alkathene LDPE polymers have peak melting temperatures between 100°C and 118°C. Alkatane High density polyethylenes, for comparison, have peak melting temperatures typically in the range of 130°C to 138°C. Alkatuff LLDPE grades have major melting peaks between 125°C to 130°C. In some LLDPEs there may be a shoulder or a secondary endotherm at a lower temperature possibly down to about 105°C; these peaks represent the linear and branched components in the molecule. The relationship between the peak melting temperature as measured by DSC and the polymer density is shown in Figure 8 for lower density polymers.

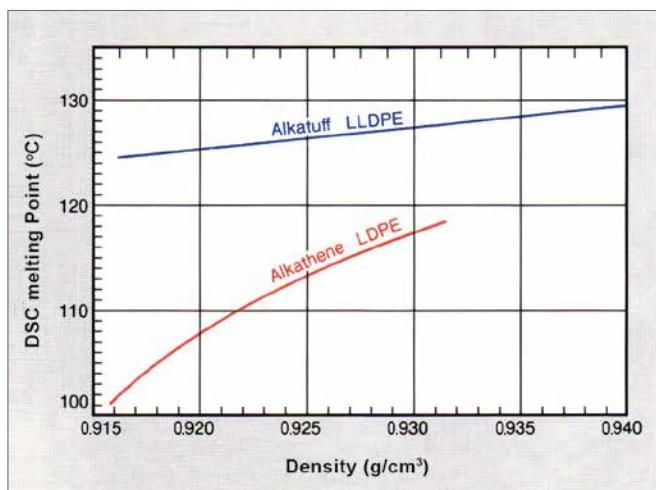


Figure 8: Melting Temperature vs. Density for lower density polyethylenes (Peak Melting Temperature Measured by Differential Scanning Calorimetry)

Above the melting temperature, the polymer is an amorphous mass which behaves as both a viscous and an elastic fluid.

Behaviour on Cooling from the Molten State

As the amorphous molten polyethylene is cooled, it begins to crystallise about nuclei in the polymer. Typical cooling curves are shown in Figure 9. As for the melting stage, crystallisation occurs over a range of temperatures. LLDPE will crystallise and solidify at higher temperatures than LDPE, and higher density linear polyethylene will typically also crystallise at higher temperatures than lower density linear polyethylene grades. The level to which the polymer is able to crystallise depends primarily on the degree of branching and the rate of cooling, but is also influenced by the molecular weight.

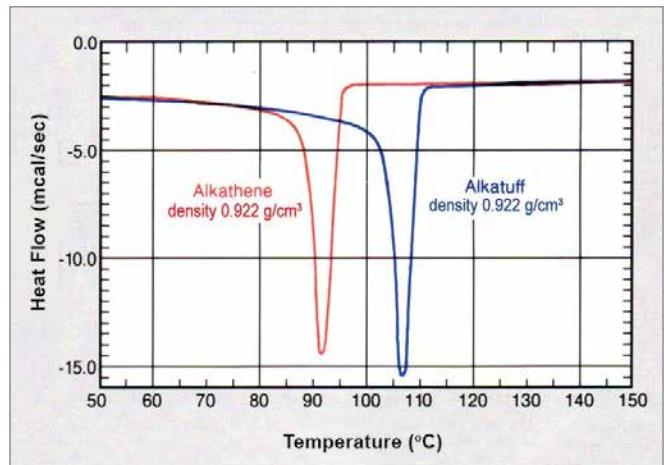


Figure 9: DSC Cooling Curves for Polyethylene of Density 0.922 g/cm³ (Cooling Rate 20°C/min)

Often it is advantageous, for example in injection moulding when cycle times can be reduced, to include nucleating agents in the polyethylene so that the crystallisation point is raised; such agents can be particularly effective in LLDPE.

The crystal structure achieved during the cooling is significantly affected by the rate of cooling – fast cooling (quenching) does not allow the spherulites to grow as much and a less crystalline lower density structure results. Slow cooling allows the crystallites to organise themselves into large spherulites, resulting in higher crystallinity and density. Some typical figures for LDPE are given in Table 2. These differences in crystalline structure have important effects on both optical and mechanical properties; increased crystallinity will increase haze and tensile strength, coupled with a reduction in impact properties.

Table 2: Variation of the Density of Polyethylene with Cooling (Production) Conditions

Cooling Condition	Density (g/cm ³)
Pellets before Processing	0.920
Cooled at 50°C/hr	0.925
Blown Film (moderate cooling rate)	0.919
Cast Film (rapid cooling)	0.916

Table 3: Variation of Density with Time at 25°C for MFI 2 Polyethylene Quenched from 190°C in Cold Water

Time after Quenching Hours	Days	Density (g/cm ³)
1.5		0.9173
6.5		0.9177
25	1	0.9183
145	6	0.9189
410	17	0.9202
3190	133	0.9198
Slow cooled from 165°C		0.9220

Polyethylene which has been cooled rapidly from the melt will undergo a gradual increase in crystallinity at room temperature and hence an increase in density. The data in Table 3 illustrates this effect, the density increasing by 0.03 g/cm³ during the first two weeks and then remaining effectively constant.

MELT FLOW (PROCESSING) PROPERTIES

Melt Processing and Rheology

One of the most important characteristics of a thermoplastic is its ability to be processed as a melt into the final shaped product, generally via extrusion or moulding. Therefore it is essential that the polymer has easy melt processing properties. An understanding of the melt flow behaviour of the polymer is advantageous in achieving this characteristic. The general term relating to melt flow is rheology.

The three major variables in polyethylene melt processing are time (i.e. output rate, line speed, etc.), temperature and pressure; none of these variables is really independent of the others.

Polymer melts will flow when subjected to forces (or stresses) which can act in both shear and extension. This flow behaviour is markedly non-Newtonian, since the flow or viscosity depends on the flow rate or extension to which the melt is subjected. Polymer melts are also elastically deformed by these stresses and some of this deformation is recovered when the stress is removed. Polymers are thus visco-elastic materials – they have both viscous flow and elastic properties in the melt. These characteristics arise because of the very long molecular chains and the very high intermolecular forces.

The rheological properties of a polymer melt are basically expressed by the melt viscosity (in both shear and extension) and the melt elasticity. These properties are usually measured as functions of shear rate (i.e. the flow rate or throughput) and the temperature of flow. They can also be influenced by the pressure, the degree of shear working, and degradation or oxidation experienced by the polymer.

Because of the basic differences in molecular structure between highly branched LDPE and linear polyethylenes, in particular in molecular weight distribution and long chain branching, there are significant variations in the rheological performance between the two. The following discussion outlines these rheological differences.

Flow in Shear

In the melt, the polymer molecules can be considered as entangled random coils. The entanglements are an impediment to the flow of the polymer. These entanglements become greater as the molecular weight and the degree of long chain branching increase. The molecular weight is the single most important parameter in determining the melt viscosity. For example, a factor of two change in molecular weight can produce up to a tenfold change in the viscosity at a given shear stress for polyethylenes of general interest.

In the steady flow of a melt through a die channel, a velocity profile is set up, with the maximum flow at the centre and negligible flow at the wall. In effect, the layers of the melt slide over each other in a shearing action. This is shear flow.

The flow behaviour in shear is generally represented by a flow curve of shear viscosity vs. shear rate, which can be measured on a rotational rheometer at low shear rates (less than 1 sec⁻¹) and on a capillary rheometer at higher shear rates. Typical flow curves for LDPE and LLDPE polymers are given in Figures 10 to 12. These flow curves demonstrate the shear thinning nature of the polyethylene, i.e. the viscosity decreases as the shear rate or flow rate increases. In addition, a comparison can be made of the viscosities of different grades of polyethylene (see Figure 11), and also of the flow at different temperatures (see Figure 12).

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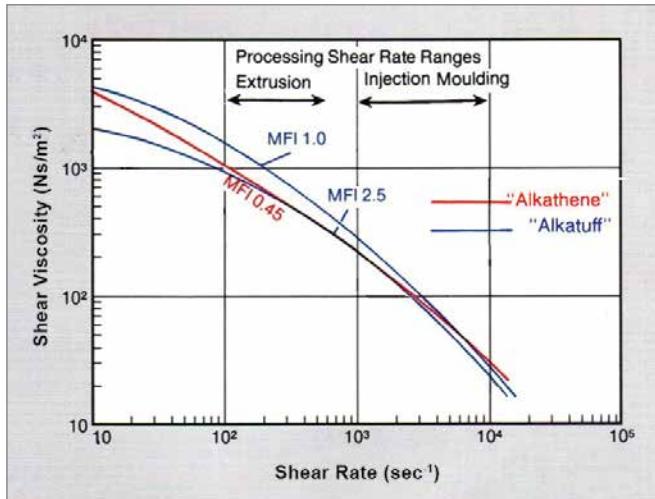


Figure 10: Variation of Shear Viscosity with Shear Rate for Alkathene LDPE and Alkatuff LLDPE Polymers at 190°C

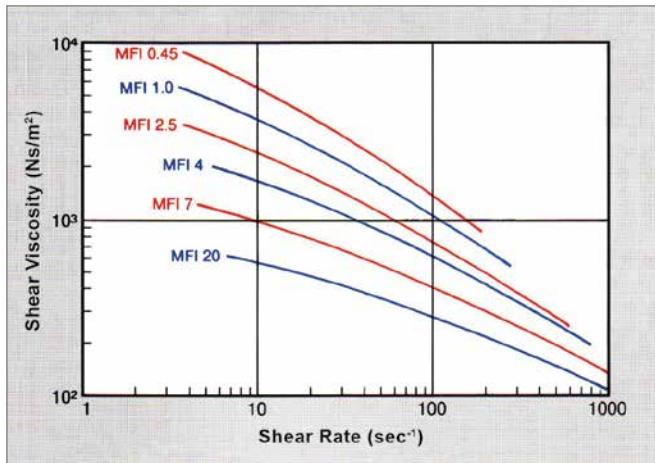


Figure 11: Comparison of Shear Viscosity vs. Shear Rate Curves for Alkathene LDPE grades with Different Melt Flow indices (Temperature = 190°C)

One significant observation is that the flow curves for different polyethylenes with the same Melt Flow Index can have different shapes – the LDPE samples have a steeper slope than that for the LLDPE examples at a shear rate of about 100 sec⁻¹. This slope of the flow curve relates to the molecular weight distribution (MWD) of the polymer, with the narrow MWD LLDPE having a flatter slope than the broader MWD LDPE. While two grades may have similar viscosities at low shear rates, for example at the low rates used in the standard MFI test, their viscosities at high shear rates typical of extrusion (100–500 sec⁻¹) or injection moulding (1,000–1,0000 sec⁻¹) may be quite different.

For example, an MFI 2.5 Alkamax mLDPE grade has higher viscosity and therefore will be harder to process by extrusion than an MFI 2.5 Alkathene LDPE grade.

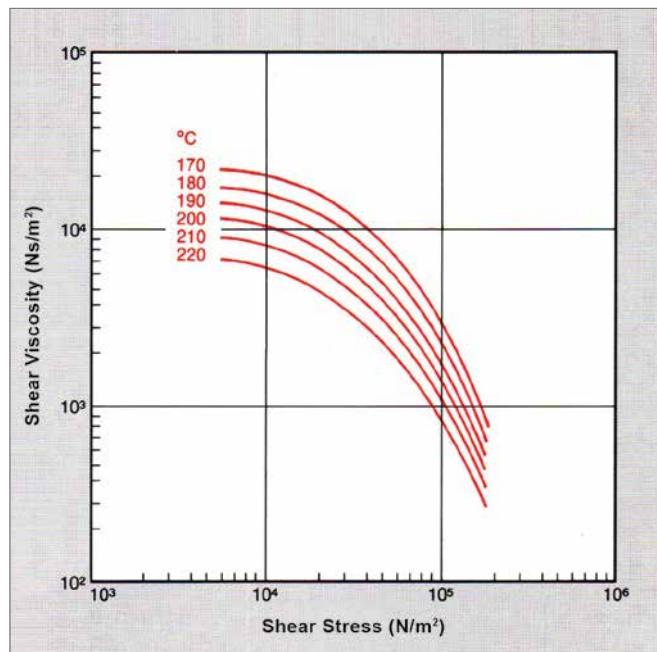


Figure 12: The Effect of Temperature on the Shear Viscosity of Polyethylene

Melt Flow Index

The shear viscosity of a polymer melt can be correlated with both the processability of the polymer and its mechanical properties in the solid state. The Melt Flow Index (MFI) test is used as a simple measure of the melt viscosity, to distinguish between different grades of polyethylene, and to provide some idea of the processability and mechanical performance of the polymer.

Using an MFI Grader, the polyethylene is melted at a temperature of 190°C and forced by a weighted piston through a small diameter capillary die under standardised conditions. The MFI is the mass of polymer (measured in grams) extruded through the die in 10 minutes under a load of 2.16 kg. This test is defined in various standards – ISO 1133, ASTM D1238, BS 2782 Method 720A, DIN 53735.

It is important to realise that this MFI value corresponds to the reciprocal of the viscosity and molecular weight, a high value implying a low molecular weight, low viscosity grade. Table 4 shows the approximate relationship between melt flow index, number average molecular weight and melt viscosity.

Table 4: Approximate Relationship between Melt Flow Index, Melt Viscosity and Number Average Molecular Weight (for LDPE with Density about 0.920 g/cm³)

Melt Flow Index	0.2	0.7	2	7	20	70	200
Melt Viscosity (Ns/m ²)	30000	10000	3000	1000	300	100	30
Number Average Molecular Weight	33500	28000	25000	21000	18000	15000	13500

A high MFI grade will be easier to process but have inferior physical properties compared with a low MFI grade. The choice of MFI for a given application is hence often a compromise between the desired properties and acceptable processability. The following lists typical MFI ranges for common processes (see Table 5):

Table 5: Illustration of the MFI Range used in specific Polymer Processes

Process	MFI Range
Injection Moulding	5 – 100
Rotational Moulding	5 – 10
Extrusion Coating	4 – 12
Film Extrusion	0.3 – 7
Blow Moulding	0.1 – 2
Pipe and Profile Extrusion	0.2 – 2

Since molten polyethylene is non-Newtonian, the MFI or viscosity measured under one set of conditions cannot be extrapolated to apply to any other set of conditions, where the melt temperature, die dimensions or melt pressure are different.

Melt Flow Index Ratio

As discussed above, the sensitivity of the shear viscosity to shear rate, i.e. the slope of the flow curve, depends on the molecular weight distribution (MWD) of the polymer. The ratio of viscosities at two shear rates is a measure of the slope and therefore is indicative of the breadth of the MWD. In practice, the Melt Flow Index Ratio (MFR) is used – this is the ratio of the MFI measured under standard conditions at 190°C with a load of 21.6 kg to the MFI measured under the same conditions using a load of 2.16 kg (e.g. MI₂/MI₂₁).

For LDPE, molecular weight distributions can vary between different grades and the MFR generally lies between 30 and 60. For LLDPE and other linear polyethylenes, the MWD is narrow and the MFR is typically between 20 and 30.

Extensional Flow

Extensional flow occurs when a melt flows through a die channel with either converging or diverging dimensions, or when it is being stretched or drawn under tension during the melt forming process. In these processes the melt is being subjected to extensional as well as shear forces.

Hence extensional flow is important in any melt stretching operations such as film extrusion and extrusion coating, and relates to the melt strength. Flow curves of extensional viscosity vs. extension or strain have been measured, and these are typically shown in Figure 13. Strain rates during blown film extrusion are typically between 0.01 and 3 sec⁻¹.

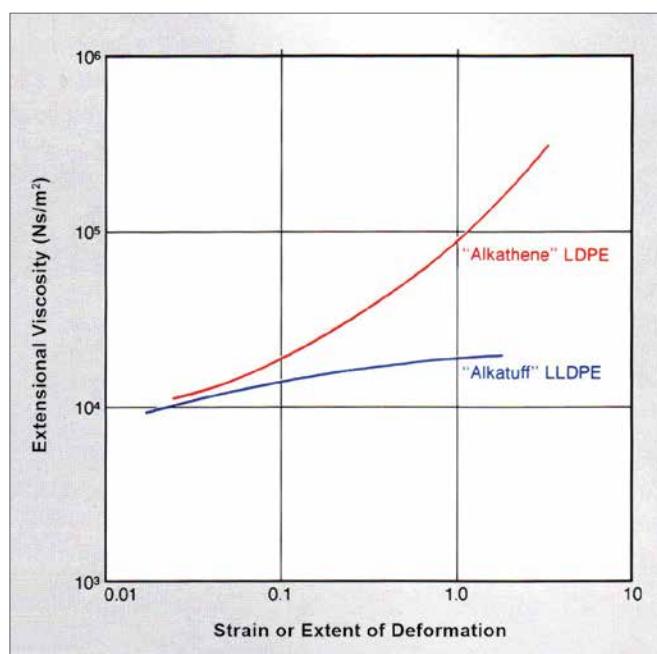


Figure 13: Extensional Viscosity of Alkathene LDPE and Alkatuff LLDPE Polyethylenes (MFI 2) at 150°C and 0.1 sec⁻¹ Strain Rate

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It is important to note that LDPE exhibits the property of tension-stiffening or strain hardening, i.e. the extensional viscosity increases with strain rate because of its broad molecular weight distribution and unique long chain branching characteristics. By comparison, linear polymers including *Alkatuff* LLDPE have a lower extensional viscosity and show a much reduced tendency to strain-harden. These differences have important implications in the processing behaviour of these polymers, especially with LLDPE in relation to bubble stability in film extrusion and draw resonance in the cast film and extrusion coating processes. The lower extensional viscosity means that LLDPE is much easier to draw down to thin gauges.

Temperature Effects

During processing, heat is applied to the polymer causing the molecules to become more mobile. The polymer softens, melts and becomes fluid. An increase in the temperature of the melt causes a decrease in its viscosity. This temperature dependence of the viscosity is illustrated for an MFI 0.3 *Alkathene* LDPE in Figure 12.

For branched polyethylene, the shear viscosity at constant stress increases by about 30% for a reduction of 10°C in the temperature in the region of 200°C. The shear viscosity of linear polyethylene like *Alkatuff* LLDPE is less sensitive to temperature, the equivalent increase in viscosity for a 10°C temperature reduction being about 20%.

Exposure of a melt to high temperatures may produce a chemical change in the polymer through thermal or oxidative degradation. This degradation can alter the viscosity of the melt at that temperature.

Pressure Effects

Polymer melts are highly compressible. Typically a 100 MPa pressure rise will cause a 10% increase in density. Pressure also increases the viscosity of melts and at a given high shear rate, the shear viscosity at a pressure of 100 MPa is about 4 times greater than that at atmospheric pressure. This 100 MPa pressure rise has the same effect on viscosity as reducing the temperature by about 50°C. The dependence of viscosity on pressure can be important in some melt fabrication processes, especially injection moulding, where very high pressures can be generated.

Melt Elasticity and Memory

It is a well-known phenomenon during extrusion that the dimensions of the extrudate are greater than those of the die from which it has emerged. This effect is known as die swell.

Die swell can be measured in terms of the swelling ratio, which is the ratio of the diameter of an extruded monofilament to the diameter of the die. For a given polymer, this swelling ratio, is dependent on shear rate, temperature and die dimensions and is a simple measure of the melt elasticity. Typical values for the swelling ratio range from 1.2 to 1.8 for *Alkathene* LDPE grades and from 1.1 to 1.4 for linear polyethylenes. Melt elasticity and swelling ratio depend considerably upon molecular weight distribution and long chain branching, hence the low values for linear polymers.

During melt flow the polymer is subjected to shear stress which forces the randomly coiled molecules to untangle and to orient themselves, most commonly in the direction of flow. When the shear stress is released, for example as the melt emerges from the die, the molecules will tend to relax elastically to their initial randomly coiled state; it is this elastic recoil which causes die swell. This elastic effect known as melt memory can, in addition to die swell, be associated with extrudate defects such as distortion and "sharkskin", frozen-in orientation and melt drawdown.

The molecules in a given molten polymer do not all recoil or relax at the same rate when the shear stress is released. The larger and more highly branched molecules take longer than the shorter molecules. If this relaxation time is longer than the time-scale of the process for the melt to drop in temperature and to solidify or freeze, then that orientation is said to be "frozen-in" and is permanent. This frozen-in orientation can have a dramatic deleterious effect on mechanical properties.

Because of its lower melt elasticity, LLDPE has much faster relaxation times and gives lower frozen-in orientation than LDPE. HDPE grades on the other hand, can vary quite significantly in melt elasticity depending on the molecular weight distribution. Bimodal HDPE grades such as *Alkadyne* HDF193B can have significantly higher melt elasticity compared to Unimodal HDPE grades of similar MFI.

Flow Defects

In the extrusion of polyethylene at low output rates, a smooth glossy extrudate is invariably obtained. However, as the output rate is increased, several flow or extrusion defects can occur. These are:

- a. A marked surface roughness characterised by a series of parallel ripples on the surface of the extrudate. This defect is commonly called sharkskin, and is associated with the rapid acceleration of the surface flow at the die exit. In its early stages, it shows as a fine mattness or loss of gloss.

This defect can occur during the extrusion of narrow molecular weight distribution polymers and, in this context, is commonly termed surface melt fracture. In film polymers this melt fracture may lead to poor optical properties. Several approaches can be used to delay the onset of surface melt fracture and these include extruding with wide die gaps, and adding a processing aid to the polymer. *Alkatuff* LLDPE and *Alkamax* mLLDPE film polymers are formulated to minimise this problem.

- b. An irregular, wavy or knobbly appearance associated with an irregular flow in the die entry region, commonly called melt turbulence, distortion or gross melt fracture. It can be markedly reduced by correctly designing the die to have a narrow entry angle, i.e. there are no dead-spots.

These defects are a consequence of the visco-elastic nature of the polymer and both may be lessened by increasing the melt temperature.

Properties of Polyethylene

Certain properties of polyethylene, for example its mechanical properties, vary with Melt Flow Index (MFI); other properties such as surface hardness and stiffness depend primarily on crystallinity or density. The electrical and thermal properties are substantially less dependent on molecular configuration and depend more on the chemical constitution of the polymer.

The choice of a polyethylene for any particular application will generally involve a compromise between the various properties. Polyethylenes of the greatest toughness are those of low MFI and low density; stiffer polyethylenes have higher densities and those that are easier to fabricate are of higher MFI.

The broad picture of the way in which the various properties of polyethylene depend on MFI, density and molecular weight distribution is summarised in Table 6.

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Table 6: Properties of Polyethylene mainly dependent on MFI, Density and Molecular Weight Distribution

Property	If the density (crystallinity) is increased	If the MFI is increased (the average mol wt is lowered)	If the molecular weight distribution is narrowed
Melt Viscosity	no effect	Much lower	slightly higher
Processability	slightly lower	Much better	lower
Vicat Softening Temperature	much higher	slightly lower	slightly higher
Melting Point	much higher	Lower	slightly higher
Heat Resistance	much higher	Lower	no effect
Minimum Sealing Temperature	Higher	slightly lower	slightly lower
Heat Seal Range	slightly wider	slightly wider	-
Tensile Strength at Yield	much higher	slightly lower	no effect
Tensile Strength at Break	Higher	Lower	no effect
Elongation at Break	Lower	much lower	no effect
Tensile Stiffness (Elastic Modulus)	much higher	slightly lower	no effect
Flexural Stiffness	much higher	slightly lower	no effect
Impact Strength	much lower	much lower	slightly higher
Brittleness Temperature	Higher	higher	no effect
Resistance to Brittleness at Low Temperature	Lower	Lower	slightly higher
Flex Life	Lower	Lower	-
Resistance to Creep	Higher	slightly lower	slightly higher
Resistance to Environmental Stress Cracking	Lower	much lower	slightly higher
Surface Hardness (Abrasion Resistance)	Higher	slightly lower	no effect
Shrinkage	higher	lower	no effect
Warpage	slightly higher	lower	lower
Resistance to Mould Sticking	higher	slightly lower	no effect
Electrical Power Factor (Tan Delta)	slightly lower	no effect	no effect
Dielectric Constant	slightly higher	no effect	no effect
Dielectric Strength	no effect	no effect	slightly higher
Film Impact Strength	lower	lower	higher
Film Tear Strength	lower	slightly lower	slightly higher
Resistance to Blocking	higher	slightly lower	no effect
Slip	higher	no effect	no effect
Optical Properties Transparency	lower	better	no effect
Haze	higher	lower	no effect
Gloss	higher	higher	no effect
Drawdown	slightly higher	much higher	slightly higher
Neck-in and Beading	higher	higher	lower
Chemical Resistance	much higher	lower	no effect
Grease Resistance	much higher	slightly lower	no effect
Liquid Absorption	much lower	no effect	-
Gas and Liquid Permeability	much lower	no effect	lower
Barrier Properties	much higher	no effect	higher
Weatherability (outdoors)	no effect	slightly lower	no effect

Typical values for other important properties of commodity polyethylenes are listed in Table 7.

Table 7: Properties of Polyethylene Largely Independent of MFI and Density (at 20°C unless otherwise specified)

Property	Value
Refractive Index	1.51
Surface Resistivity (at 75% R.H.)	$> 4 \times 10^{14}$ ohm
Volume Resistivity	approx. 10^{19} ohm cm
Power Factor	0.00005 – 0.0002
Permittivity (from 50 to 1010 Hz)	2.3
Dielectric Strength at 50 Hz	20 kV/mm
Thermal Conductivity	0.34 W / m K
Specific Heat (at 20°C)	2.3 kJ/kg K
Specific Heat (120 – 140°C)	2.5 kJ/kg K
Coefficient of Linear Expansion	2.2×10^{-4} cm/cm K
Compressibility at 60°C (between 0.1 – 10.13 MPa)	11.6 m ² /N
Calorific Value	406 kJ/g
Decomposition Temperature (in vacuo)	280 – 300°C

LIMITATIONS OF TEST DATA

Before discussing in detail the physical properties of polyethylene which are dependent on MFI or density, there are some important points to be explained. Many of the physical properties of polyethylene are very sensitive to the conditions of testing and to the method of fabrication of the test specimen. For these reasons the data given are typical values and may not necessarily reflect properties experienced in practice with extruded or moulded products.

Effect of Temperature

When the temperature of solid polyethylene is raised, the molecules gain more mobility and the sample becomes more flexible. For this reason, many properties are very dependent on the temperature under consideration. Because of this temperature sensitivity, testing of physical properties entails close temperature control. If practicable, the testing of an article should be carried out at a temperature similar to that experienced in service, although in some applications, elevated temperatures may be used to accelerate the effects.

Effect of Rate of Testing

The mechanical properties of all thermoplastics are time-dependent as a necessary consequence of their long chain structure. This structure resists deformation but the resistance decays as the time of testing is prolonged.

For example, an experiment involving short-time loading or high-frequency loading gives values of elastic modulus substantially higher than those obtained from a similar test carried out under conditions of slower deformation. This phenomenon applies to polyethylene, and it is necessary, therefore, before applying quoted data to any particular design problem to ensure that the conditions of testing (i.e. rate of strain, duration of loading, etc.) are similar to those that will be met in service.

Effect of Strain

Values of elastic moduli calculated from the deformation of a polyethylene specimen are found to decrease as the deformation, or strain, increases.

Measurements are usually made under conditions involving small strains and so give high values of 'stiffness', but it is generally impossible to give a simple correlation between moduli determined under different conditions.

Effect of Specimen Fabrication

Although the properties of a fabricated article depend primarily on the properties of the polymer from which it is made, they also depend on the method and conditions of fabrication. The rate of cooling to the solid state will determine the spherulite size and, especially with the less branched polymers, the final density of the fabricated article. In addition, the molecules of the polymer are oriented during the fabrication process. The polymer may freeze before relaxation can take place, leaving frozen-in strain in the final article. Variations in spherulite size, density and frozen-in strain may affect the results of any particular test.

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MECHANICAL PROPERTIES

Introduction

In most practical applications, articles made from polyethylene are liable to be pulled, bent, twisted, squeezed, impacted or mechanically deformed in some way during service. Some knowledge of how the article withstands such treatment is essential. In practical terms, there is a need for information on the tensile, flexural, torsional, compressive and impact behaviour. This information is generally in the form of the measured deformation (or strain) of the material in response to an applied load (or stress); the ratio of stress/strain is called 'modulus' and this is a measure of the stiffness of the material.

The general form of the curve showing stress versus deflection for polyethylene test specimens is shown in Figure 14. The test specimen is stretched or bent (i.e. in tension or flexure) until failure occurs. Typically four clearly defined regions of the curve are observed.

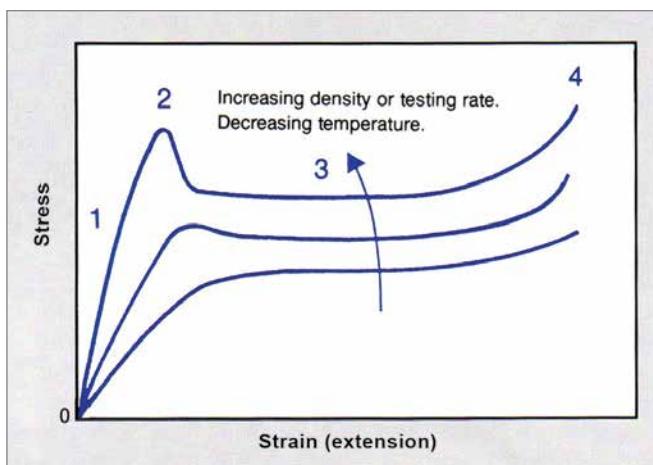


Figure 14: Typical Stress/Strain Curves for Polyethylene

Region 1: Stress increases almost linearly with extension.

Region 2: The "yield point".

Region 3: Further extension at approximately constant stress – "cold drawing".

Region 4: The "break point" – final rupture.

In region 1, the stress increases almost linearly with extension. Specimen deformation is mostly recoverable after removal of the stress, hence this is the useful range of stress and strain for most applications. The slope of this part of the curve is a measure of the elastic modulus of the polymer.

Region 2 corresponds to the "yield point", associated with the commencement of yielding or necking in the test specimen.

After yielding, further extension or "cold drawing" usually occurs at approximately constant stress (Region 3). During this process crystallite reorientation takes place. When the polymer chains approach full alignment, the stress in the sample increases until final rupture occurs (Region 4).

The precise shape of the stress versus extension curve is affected by the grade of polymer and conditions of test as indicated in Figure 15. Test specimen preparation procedures are closely controlled by international standards, in order to reduce problems of specimen variability and to avoid fine surface imperfections which may cause premature failure.

It should be noted that while mechanical test data is useful to compare the properties of different grades of polyethylene under different preparation or testing conditions, this data may not be typical of real life. If data is required for engineering design purposes, then specimens must be prepared which are representative of the intended final article and these must be tested under conditions representative of the end-use environment.

Tensile Behaviour

Tensile properties are measured on a tensile testing machine according to procedures outlined in standards such as ISO R527, ASTM D638, BS 2782. Information which can be derived from the resulting stress/strain curves includes: yield stress and strain, tensile stress and elongation at break, and tensile modulus (often measured as the 1 or 2% secant modulus). The energy-to-break, i.e. the area under the stress/strain curve, is sometimes quoted.

Typical stress/strain curves at different temperatures between -65°C and 75°C for Alkathene LDPE of MFI 2.0 and density of 0.920 g/cm³ are shown in Figure 15.

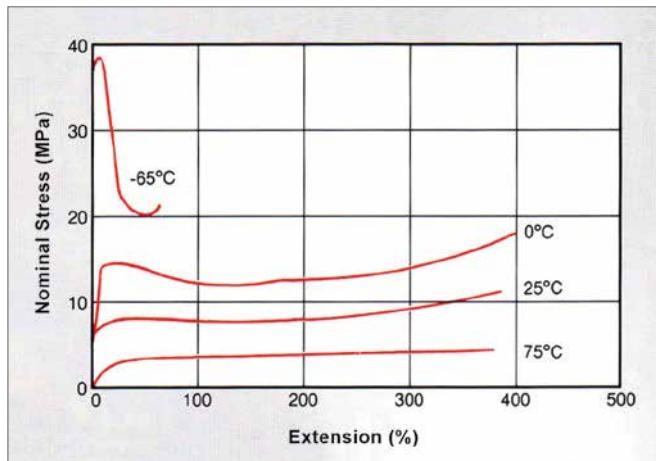


Figure 15: Effect of Temperature on Stress/Strain Curves for Alkathene LDPE of MFI 2, Density 0.920 g/cm³ (Strain Rate 200% per minute)

For most Qenos grades, the yield stress and yield strain are virtually independent of molecular weight (MFI) with a slight decrease as MFI is increased. However yield stress is very dependent on testing rate, temperature, and polymer density. The yield strain of polyethylene is typically between 8% and 20% at 20°C.

The initial slope of the stress/strain curve represents the tensile modulus (or stiffness) of the polyethylene. In general, the stiffness of the polymer increases with density. This greater stiffness can be utilised in many applications by down-gauging for a given stiffness or rigidity, but care must be taken to avoid inferior yield properties with the thinner product.

After yielding in a ductile manner, a polyethylene test specimen can be stretched to many times its original length, typically 300 to 1,000%. The ultimate elongation at failure is dependent on crystallinity and molecular weight, decreasing with both increasing density and MFI. Linear polyethylenes typically have greater ultimate elongation than LDPE.

The ultimate tensile strength at break is mainly dependent on the MFI, and decreases as the MFI increases.

Creep in Tension

Over time, finished goods produced from polyethylene, often exhibit a very slow plastic deformation known as creep. Creep resistance is measured by determining the deformation in test specimens over a long period of time for several levels of applied stress. The level of creep will increase with loading time, the applied stress and temperature.

Because polyethylene is not generally used as an engineering material, interest in its creep characteristics is usually limited in practice to small deformations of much less than 5%. Creep under these conditions is not very sensitive to molecular weight, but is very dependent on polymer density. Figure 16 shows the creep or deformation with time at 20°C for three grades of polyethylene of different density, under the same stress of 4 MPa. Because the crystallinity (and hence density) of polyethylene depends on the rate of cooling and can change slowly for many hours after moulding (compare Table 3), the long-term creep strain is very dependent on the thermal history and storage conditions of the specimen.



Figure 16: Creep in Tension at 20°C against Time, for Three Grades of Polyethylene with Different Density, under a Stress of 4 MPa

When the applied stress is removed, some of the creep strain is recoverable, but this recovery is also time dependent. The degree of long term recovery can be virtually complete from low stresses involving no more than 2% maximum strain, but the recovery time will be at least ten times as long as the period of applied load. The degree of ultimate recovery decreases for higher stress conditions.

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Behaviour in Compression

For small deformations of less than 1%, the behaviour of polyethylene in compression is very similar to that in tension.

Flexural Behaviour

Flexural properties can be measured by means of standard bending tests, e.g. ISO 178, ASTM D790. In general the effect of factors such as polymer density, temperature, time, processing conditions, etc. are very similar for flexure as for tension.

Impact Properties

In the vast majority of practical applications, low density polyethylene fails in a ductile manner, i.e. it yields before breaking. It is generally considered a 'tough' plastic and impact resistance is not normally a serious problem. However, failures can occur before the yield point under extreme conditions involving one or more of the following factors:

- Presence of sharp notches, corners or rough edges
- Poor processing, involving high frozen-in stresses or weld lines
- Very rapid loading, e.g. 'explosive' rates at room temperature or normal impact loading at low (sub-zero) temperatures
- Long loading periods, particularly at high temperatures or in the presence of certain (stress-cracking) fluids
- Low temperatures
- Use of low molecular weight polymer (high MFI)

In laboratory evaluations of the impact properties of polyethylene, it is necessary to test samples with sharp notches (tip radius 0.25 mm) and low temperatures (-15°C or below) in order to obtain brittle fracture. Table 8 shows the effect of notch-tip radius on the embrittlement temperature or low temperature brittleness point for polyethylenes of differing MFI. The tough/brittle transition temperature is the temperature at which 50% of the test specimens break when flexed rapidly at each of a range of temperatures. For a blunt notch, the notch sensitivity is very dependent on MFI with the higher MFI being worse; for very sharp notches the effect of MFI has disappeared.

Table 8: The Effect of Notch-tip Radius and MFI on the Tough/Brittle Transition Temperature of LDPE (Based on ISO Test Method 179)

MFI (g/10min)	Density (g/cm ³)	Tough/brittle Transition Temperature (°C)		
		Notch-tip Radius		
		Razor cut	0.25 mm	2 mm
20	0.916	+5	-18	-38
7	0.917	+ 5	-24	-47
2	0.918	+ 5	-28	-64

The impact strength of polyethylene depends on both the MFI and density, and polymers at the low end of the MFI and density spectrum have the greatest toughness. As the density of the polymer increases it becomes more brittle. In general LLDPE is expected to give greater impact performance than LDPE for a given MFI and density, and mLLDPE even higher impact performance than LLDPE.

Fracture Mechanics Analysis

Toughness and ductility of polyethylenes can also be usefully expressed by a fracture mechanics analysis of fracture data. Fracture generally occurs because of inherent flaws in a material. When these are subjected to a force, a region at the edge of the flaw becomes deformed. The size of the deformed region (the plastic zone) relative to the dimensions of the component will govern the type of ensuing fracture behaviour, e.g. a large plastic zone size leads to ductile behaviour, a small plastic zone leads to brittle behaviour. Linear elastic fracture mechanics provides an expression relating the plastic zone size and the ratio of the stress field intensity factor (K) to the yield stress; by measuring these quantities, the ductility of the material can be described.

Generally experience of fracture behaviour indicates that K increases with decreasing MFI, while the yield stress increases with density. Typically plane strain values for K will be in a range up to about 4 MPa.m^{1/2} whilst short term yield stress is in a range up to about 20 MPa.

Environmental Stress Cracking Resistance (ESCR)

When polyethylene is highly stressed, either by external deformation or internal frozen-in strain and is in contact with certain materials, cracking may occur. This happens even though these materials are poor solvents for polyethylene or are only slightly absorbed.

This phenomenon is known as environmental stress cracking and may be caused by liquids or vapours (particularly the vapours of volatile polar liquids).

In the absence of these materials the polyethylene might withstand the same stress indefinitely. Conversely, unstressed samples might readily withstand cracking when in contact with the active agents.

Table 9 lists some of the active environments which could be polar organic compounds, surface active agents (e.g. detergents), or silicone compounds.

Table 9: Classification of Materials as Stress Cracking Agents for Polyethylene

Active	Inactive
Alcohols	Water
Liquid hydrocarbons	Polyhydric alcohols
Organic esters	Sugars
Metallic soaps	Hydrolysed protein
Sulphated and sulphonated alcohols	Rosin
	Selected asphalts
Polyglycol esters	Selected saponins
Silicone fluids	Acid and neutral inorganic salts

The resistance to stress crack failure is determined by four factors:

- Type of polyethylene
- Activity of the environment
- Magnitude of the applied stress
- Magnitude of residual (e.g. frozen-in) strain in the product.

Injection moulded articles are particularly vulnerable to this problem around the sprue area, because of the high degree of molecular orientation or frozen-in strain introduced into the moulding during the mould filling operation.

Resistance to environmental stress cracking is a function of molecular weight, density and structure of the polymer. The probability of environmental stress cracking decreases when both the MFI and the density decrease. Thus a polymer grade of MFI 20 is rapidly cracked by a wide variety of environments whereas one of MFI 0.3 may be unaffected under the same conditions. A polyethylene with a density of 0.918 g/cm³ is more resistant than a grade with a similar MFI but density of 0.924 g/cm³.

For a given MFI and density, LLDPE has a much superior environmental stress crack resistance than LDPE. In linear polyethylenes, the distribution and length of the side branches has a profound effect on the environmental stress crack resistance. Some typical ESCR values for Alkathene LDPE and Alkatuff LLDPE polymers are given in Table 10. The effects of density and melt index on the ESCR of HDPE grades in shown in Table 11.

Table 10: Typical Values for the Environmental Stress Crack Resistance of Alkathene LDPE and Alkatuff LLDPE Grades

MFI	Density g/cm ³)	Environment “Teric” GN9 concentration	ESCR F50 value
LDPE			
60	0.919	10%	7 min
30	0.920	10%	8 min
20	0.920	10%	20 min
8	0.926	10%	7 min
1.7	0.919	10%	5 hr
7	0.918	22%	30 min
2.5	0.921	22%	35 min
1.7	0.918	22%	60 min
0.5	0.924	22%	2.4 hr
0.3	0.926	22%	1.1 hr
0.3	0.921	22%	30 hr
LLDPE			
20	0.934	10%	0.5 hr
20	0.924	10%	
5	0.935	10%	5 hr
4	0.925	10%	>200 hr
1	0.919	10%	300 hr
50	0.926	100%	>1000 hr
20	0.924	100%	3 hr
20	0.920	100%	24 hr
12	0.926	100%	>1000 hr
5	0.935	100%	11 hr
2	0.920	100%	>500 hr

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Table 11: Typical Values for the Environmental Stress Crack Resistance of Alkatane and Alkadyne HDPE Grades

	HDPE 1	HDPE 2	HDPE 3	HDPE 4	HDPE 5
Density g/cm ³	0.95	0.963	0.955	0.955	0.958
MFI g/10 min	0.3	0.25	36	10	0.3 (M ₅)
ESCR					
ESCR F50 value hours/ Condition B	400	15	2	3	>1000
Moulding Process	Blow	Blow	Injection	Injection	Extrusion
Applications	Industrial Containers	Containers	Cap/Closures	Housewares	Pipe

Resistance to environmental stress cracking is determined by the so-called Bell test and this method is described in the standards (ISO 4599, ASTM D1693). In this test, rectangular moulded polyethylene specimens are notched and bent in a standard frame, and placed in a standard detergent solution at 50°C; the time for 50% of the specimens to fail is measured and quoted as the F50 value.

In spite of the undoubtedly correlation between the environmental stress cracking test and actual service conditions, it is nevertheless very difficult to make any general recommendations. The size of a moulding together with the conditions and method of fabrication may well completely dominate the resulting performance for a particular application.

Surface Hardness

The hardness of polyethylene relates to its modulus of elasticity. It is thus essentially determined by the polymer crystallinity and density, with hardness values increasing as the density is raised. Molecular weight has a small influence on hardness, with values being slightly lower as the MFI is raised.

There are various methods of measuring hardness but the Shore D Hardness test (ISO 868, ASTM D2240-) is appropriate for polyethylene. Values range from 40 to 50 for LDPE, 50 to 60 for MDPE, and 60 to 70 for HDPE.

THERMAL PROPERTIES

The thermal properties of polyethylenes do not vary significantly with molecular weight and density, the exception being the melting point. The data given in Table 12 lists some average thermal properties measured at 20°C.

Table 12: Thermal Properties of Polyethylene at 20°C

Property	Value
Thermal Conductivity	0.34 W/m K
Specific Heat (at 20°C)	2.3 kJ/kg K
Specific Heat (above melting point)	2.5 kJ/kg K
Coefficient of Linear Thermal Expansion	2.2 × 10 ⁻⁴ cm/cm K
Decomposition Temperature (in vacuo)	280 – 300°C
Calorific Value	406 kJ/g

Vicat Softening Point

The temperature at which polyethylene softens – as distinct from melts – varies with both molecular weight and density. The most convenient softening point test is the Vicat penetration test (ISO 306, ASTM D1525). The Vicat softening point occurs at a lower temperature than the crystalline melting point as measured by Differential Scanning Calorimetry (compare Figure 8).

Typical Vicat softening points for a range of *Alkathene* LDPE and *Alkatuff* LLDPE grades of different MFIs and densities are given in Table 13. The temperature defined by this test gives a practical guideline to the upper temperature limit at which a stressed sample of polyethylene may be used.

Table 13: Typical Vicat Softening Points for **Alkathene LDPE**, **Alkatuff LLDPE**, **Alkatane HDPE** at Various MFI and Density

	Vicat Softening Point (°C)								
	Alkathene LDPE			Alkatuff LLDPE			Alkatane HDPE		
	Density (g/cm³)								
	0.920	0.925	0.930	0.920	0.925	0.935	0.954	0.955	0.960
MFI (g/min)									
0.35							127		
0.7		103		112	114				
1.0	96.5			109			127	129	
2.5	92.5	104			118.5				
4.0							125		
5.0 – 7.0	88.5	93			116				
20.0	84.0	97	98	104					

Thermal Conductivity

The thermal conductivity of plastic materials (i.e. their ability to conduct heat) varies with the degree of crystallinity and hence density. Figure 17 shows the thermal conductivity of several grades of polyethylene with different densities as a function of temperature. At 20°C the thermal conductivity of low density polyethylene is about 0.34 W/m K.

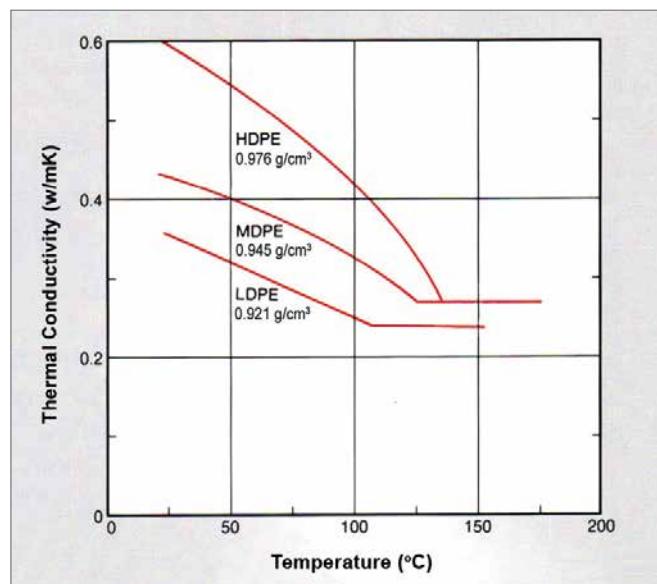


Figure 17: Thermal Conductivity of Several Polyethylenes of Specified Densities

Thermal Diffusivity

In any calculations of the heat transfer or temperature profiles in a material under non-steady state conditions, an important quantity is the thermal diffusivity. This parameter is related to the other thermal properties by the equation:

$$\alpha = k / (\rho \cdot C_p)$$

Where α = Thermal Diffusivity

k = (Thermal Conductivity)

ρ = Density

C_p = Specific Heat

Figure 18 shows the thermal diffusivity of Alkathene LDPE, Alkatuff LLDPE and Alkatane HDPE as a function of temperature.

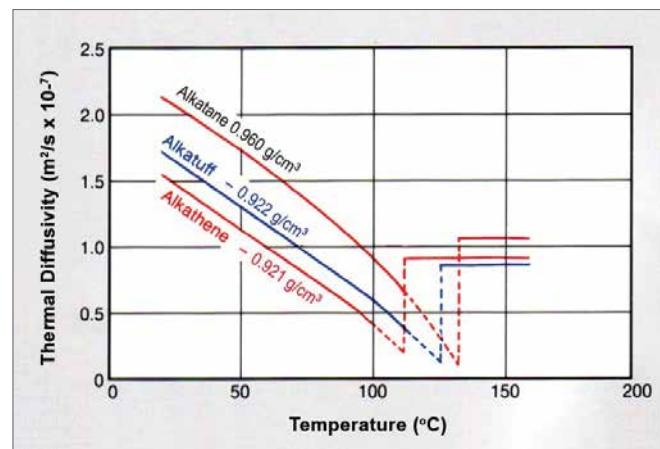


Figure 18: Thermal Diffusivity of Alkathene LDPE (density 0.921 g/cm³), Alkatuff LLDPE (density 0.922 g/cm³) and Alkatane HDPE (density 0.960 g/cm³)

1 GENERAL PROPERTIES

Coefficient of Thermal Expansion

The linear coefficient of thermal expansion of low density polyethylene is approximately $2 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$ at 20°C. This coefficient, however, does not remain constant with temperature, but increases to about $3.5 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$ at 80°C.

A related property is the specific volume expansion which, for an isotropic material, is taken to be three times the linear coefficient.

The specific volume (reciprocal of the density) is also temperature dependent, as indicated in Figure 19 for both low and high density polyethylene. An important point to note is that the melt density of low density polyethylene is much lower than the solid density, being 0.760 g/cm³ at 200°C.

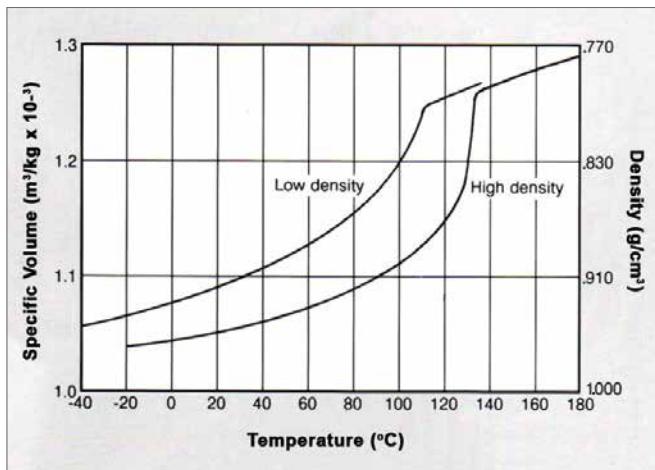


Figure 19: Variation of Specific Volume with Temperature for Low and High Density Polyethylene

ELECTRICAL PROPERTIES

The electrical properties of polyethylene are outstandingly good, it is one of the best insulating materials available. It has low dielectric losses, low permittivity, high resistivity, high dielectric strength and good resistance to tracking. With such electrical properties, it is used in many insulating applications in the cable industry, from submarine telecommunication cables to low power electrical distribution cables and telecommunications wiring.

These electrical properties do not vary appreciably with MFI and only slightly with density, and are very similar for branched and linear polyethylenes. Typical values (determined at 20°C) are given in Table 14.

Table 14: Electrical Properties of Polyethylene at 20°C

Property	Test Method	Value
Dielectric Loss (Power Factor)	IEC 250	50-200 microradians
Permittivity for 920 kg/m ³	IEC 250	2.285
Permittivity for 940 kg /m ³	IEC 250	2.325
Volume Resistivity (1000 sec polarisation)	IEC 93	approx. 1019 ohm cm
Surface Resistivity (at 75% R.H.)	IEC 93	> 1016 ohm
Dielectric Strength under oil, specimen 3 mm thick	IEC 243	20 kV/mm
Comparative Tracking Index	IEC 112	> 600

Permittivity and Dielectric Loss

The dielectric losses in polyethylene arise from the interaction of the polar groups in the material with the electric field. Some of these groups are intrinsic to the polyethylene molecule, while others arise from purposely added stabilisers, pigments, carbon black, etc. and from adventitious process and catalyst residues.

Additive-free low density polyethylene has a very low dielectric loss, amongst the lowest of any plastics, and virtually at the limits of measurement resolution. Values for the dissipation (power) factor or loss angle ($\tan \delta$) for a 0.923 g/cm³ density polyethylene at 23°C remain below 100 micro radians (0.0001) up to 10⁷ Hz, and then generally increase with a slight maximum at 10⁹ Hz (see Figure 20). The dielectric loss does not change markedly with temperature in the range 20 to 80°C, but decreases slightly with an increase in density.

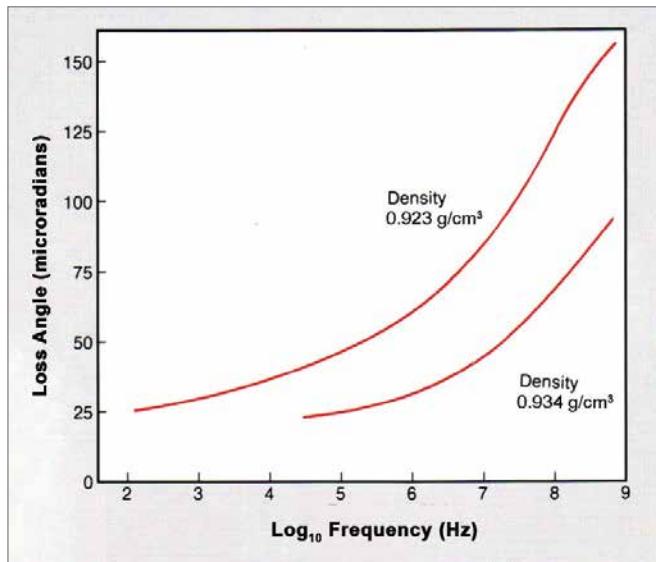


Figure 20: Dielectric loss (loss angle) of Polyethylene as a function of Frequency, Measured at 23°C

The dielectric loss is very sensitive to slight degrees of oxidation, such as may occur if processing has been faulty or if antioxidants have not been used correctly. Excess antioxidant and the wrong choice of antioxidant are both detrimental to the loss properties. Grades of polyethylene recommended for cable applications contain antioxidant sufficient to protect them during normal processing. The presence of any polar additives in the polymer will also markedly increase the values for tan delta. Dielectric loss properties are very sensitive to the small level of catalyst residues which may be present in polymers such as Alkatuff LLDPE made by low-pressure polymerisation processes.

The permittivity or dielectric constant of polyethylene (the ratio of the capacitance of polyethylene as the dielectric compared with the equivalent capacitance of a vacuum) increases slightly with increasing density, by about 0.0002 per 0.01 g/cm³; values are 2.285 for polymer of density 0.920 g/cm³ and 2.325 for polymer of density 0.940 g/cm³ (measured at 20°C and 10 kHz). Permittivity does not vary appreciably with frequency but does decrease slightly with increasing temperature, the temperature coefficient at 20°C being approximately -0.0012 per °C.

Because the water absorption of polyethylene is very low, its dielectric properties are not affected appreciably by humidity.

Dielectric loss and permittivity properties can be measured according to the methods in IEC 250 and ASTM D150.

Volume and Surface Resistivity

The resistivity of polyethylene is so high that true measurements are difficult to make. It increases with time of electrification due to polarisation effects. At testing times greater than 1,000 seconds, values of 10¹⁶ to 10¹⁷ ohm-m (at 20°C) are obtained for the volume resistivity.

The surface resistivity is strongly affected by the nature of the surface being measured, e.g. its cleanliness, surface finish and any additives which have exuded to the surface. The values obtained for various grades of polyethylene are of the order of 10¹⁶ ohms.

Measurement of the surface resistivity is often used to assess the effects of antistatic or antifog additives in film made from polyethylene. Addition of these additives results in a significant decrease in the surface resistivity values, and these values are very sensitive to the relative humidity.

Volume and surface resistivity are measured according to the test methods given in IEC 93 or ASTM D257.

Dielectric Strength

The dielectric strength of polyethylene subjected to either DC or low frequency AC voltages depends very markedly on the nature of the specimen and the conditions of testing. The satisfactory performance under high electrical stress depends on achieving a good contact between the polyethylene and the conductor. Without this, partial discharges will occur between the conductor and the polyethylene, leading to heat generation, degradation of the plastic and ultimate breakdown of the component. In practice, electrical components insulated with polyethylene should be designed for freedom from discharges.

Dielectric strength values measured according to standard test methods such as IEC 243 or ASTM D149 are short-term values obtained in the presence of excessive discharging and therefore cannot be used directly as design criteria.

1 GENERAL PROPERTIES

CHEMICAL RESISTANCE

Introduction

Polyethylene is one of the most stable and inert polymers exhibiting very high resistance to chemical attack making it particularly useful in a wide range of applications for use with chemicals.

In general, polyethylene is resistant to attack by alkalis, aqueous solutions, non-oxidising acids, and to a lesser extent by concentrated oxidising acids, all of which cause corrosion to metals; however, they may be affected by organic solvents which usually have little, if any, effect on metals. At room temperature, they are almost insoluble in all organic solvents although some absorption, softening or embrittlement may occur. At temperatures above 70°C lower density polyethylenes dissolve in common solvents such as xylene, toluene, amyl acetate, trichloroethylene, paraffin and turpentine, but are not dissolved by glycerine, ether, carbon disulphide, acetone or linseed oil.

The lower the MFI and higher the density, the better is the resistance to chemical and solvent attack. It is therefore important that polyethylene grades of the lowest MFI consistent with ease of fabrication are used for chemical applications.

For further details on the chemical resistance of Genos polyethylene grades contact your Technical Service Representative.

Water Absorption

Polyethylene is very resistant to water and water vapour and has one of the lowest water absorption values of all commercial plastics. The absorption of water after immersion for one year at room temperature is only 0.15% by weight when measured on a disc 1 mm thick and 53 mm in diameter. The amount of water absorption increases with both time and temperature, the equivalent absorption at 50°C being about 0.5% after 6 months' immersion. With water immersion at high temperatures, oxidation of the polyethylene may become an issue with prolonged exposure.

As indicated later, polyethylene provides one of the best water vapour barriers available and is able to maintain flexibility and water resistance even when flexed repeatedly at low temperatures.

Resistance to Oils

All oils affect polyethylene to some extent. Mineral oils have the greatest effect; at elevated temperatures they dissolve the polymer and at lower temperatures they

absorbed, causing swelling, discolouration and, in the extreme, disintegration. Vegetable and animal oils do not typically have such a pronounced effect.

Table 15 shows the absorption of various vegetable and animal oils by an LDPE grade of MFI 2, density 0.917 g/cm³. With all oils, absorption and deterioration are less marked for polyethylenes of higher molecular weight (i.e. lower MFI) and higher density. *Alkatuff* LLDPE would be expected to be slightly more resistant to oil absorption than *Alkathene* LDPE.

Table 15: Absorption of Vegetable and Animal Oils by LDPE (MFI 2, density 0.917 g/cm³)

Oil	Percent Weight Increase in one month		
	20°C	40°C	80°C
Transformer oil	6.0	10.0	40.0
Tallow	0.3	0.8	7.4
Ground-nut oil	0.1	0.4	5.5
Whale oil	0.1	0.5	5.0
Sardine oil	0.1	0.4	3.5
Linseed oil		<0.1	-

Resistance to Solvents and Organic Chemicals

At temperatures below 60°C, lower density polyethylenes slowly absorb solvents and swell but do not dissolve to any appreciable extent. Above this temperature, their solubility in hydrocarbons and halogenated hydrocarbons rises sharply, as shown in Figure 21. Absorption, swelling and solubility are lower for higher density and lower MFI polyethylenes. Table 16 shows the equilibrium absorption of various solvents by different grades of LDPE at 50°C.

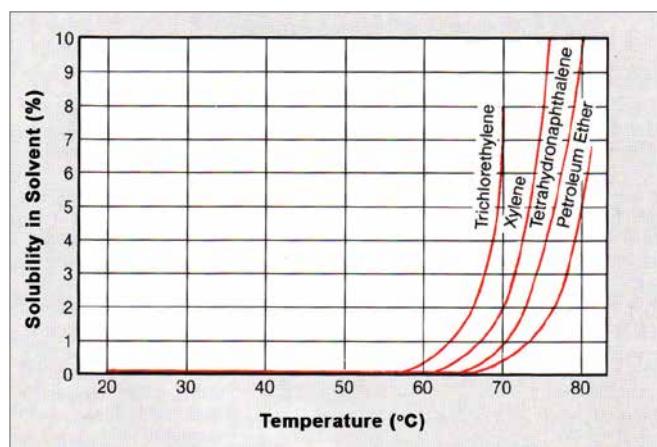


Figure 21: Variation of Solubility of Polyethylene (MFI 20, density 0.920 g/cm³) with Temperature and Solvent

Table 16: Equilibrium Absorption of Solvents by Various Grades of LDPE at 50°C

MFI/Density	Weight Increase (%)			Volume Increase (%)		
	0.3/0.920	2/0.918	20/0.916	0.3/0.920	2/0.918	20/0.916
Solvent						
Methanol	<0.01	<0.01	<0.01	Nil	Nil	Nil
Ethyl Acetate	4	5	6	6	7	8
Petroleum Ether	21	28	38	29	30	63
Benzene	26	34	44	30	43	51
Xylene	30	40	53	33	44	71
Trichloroethylene	74	100	143	51	75	90
Carbon Tetrachloride	81	110	155	59	70	96

Polar liquids such as alcohols, organic acids, esters, amines, phenols and nitro-compounds are poor solvents even at high temperatures and do not cause swelling at low temperatures. They may, however, cause environmental stress cracking. For further details contact your Technical Service Representative.

Certain organic compounds containing sulphur, and sulphur itself, are slowly absorbed by polyethylene and may adversely affect its electrical properties.

Resistance to Inorganic Chemicals

Polyethylene is not, in general, attacked by aqueous solutions of inorganic salts at normal temperature conditions. Concentrated solutions of oxidising chemicals such as hydrogen peroxide (30%) and potassium permanganate may cause some oxidation.

The only acids which affect polyethylene are those which have an oxidising effect at high concentrations. Thus nitric acid at concentrations greater than 30% can cause blistering, the attack being more severe at higher temperatures. Sulphuric acid can be used in contact with polyethylene up to 70% concentration. Hydrochloric acid and chromic acid plating solutions have little effect.

Polyethylene is highly resistant to alkalis, remaining unaffected by all concentrations of sodium and potassium hydroxides even at 60°C, although environmental stress cracking may occur under some conditions.

Liquid and gaseous halogens attack polyethylene slowly in the cold, but more rapidly at higher temperatures, and may cause discolouration and change in properties. Dilute solutions of chlorine and the various bleaches have little or no effect on polyethylene. Bromine and iodine are absorbed and diffuse through the polymer with the consequent degradation of the mechanical properties.

OXIDATIVE STABILITY

Oxidation of Polyethylene

Polyethylene begins to decompose slowly in vacuo or in an inert atmosphere at about 300°C and more quickly at higher temperatures, to give breakdown products consisting chiefly of low molecular weight hydrocarbons. Above 350°C gaseous products are evolved with butylene being the main component; depolymerization to ethylene does not occur.

On prolonged heating in air, polyethylene is oxidised like all other hydrocarbons, the rate of oxidation depending on the temperature. For samples stored in the dark at 20°C, no significant changes in properties have been observed after several years. As the temperature rises, so the useful life of unstabilised polyethylene decreases from years to the order of minutes at processing temperatures. The oxidation proceeds after an induction period where properties remain unchanged; this induction time can be used as a measure of the useful life of the polymer. Figure 22 shows oxidation induction curves obtained on a DSC for unstabilised and stabilised grades of polyethylene.

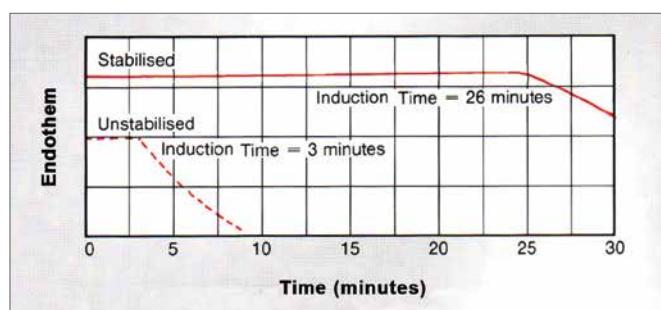


Figure 22: Thermal Oxidation of Polyethylene at 190°C in Oxygen, using a Differential Scanning Calorimeter

1 GENERAL PROPERTIES

The course of the oxidation is shown by chemical change, manifested initially by increases in the dielectric loss angle (power factor) arising from the formation of polar groups (shown as carbonyl groups by infra-red spectroscopy) and the development of a rancid odour. Melt viscosity then increases (MFI decreases) because of cross linking. Eventually the low temperature brittleness deteriorates when chain scission reactions predominate, with a loss in flexibility and extensibility. Finally, extensive discolouration and chemical decomposition with a loss of volatile products can take place.

The rate of oxidation is independent of molecular weight but dependent on the molecular structure. The point of first attack is the tertiary carbon atoms which occur in branched structures. Hence, for pure polymer, the higher density less branched polyethylenes would be expected to oxidise more slowly than lower density materials.

Because of their different branching structures, LDPE and linear polyethylenes give different rates of oxidation with, in general, LDPE being the more stable. However, this comparison is not simple because linear polyethylenes will contain a very small level of metallic catalyst residues (LDPE does not) and higher processing temperatures are often required for linear polyethylenes because of its more difficult processing properties; both of these factors will contribute to lower oxidative stability.

Stabilisation of Polyethylene

In practice, antioxidants and stabilisers are included in many polyethylene formulations to inhibit oxidation, to give protection during processing and fabrication, and to extend the useful life of the products. These antioxidants have little or no adverse effect on the other properties of the polyethylene. Different stabilisers are used for different functions - processing stabilisers to protect against oxidative degradation during processing of the polymer, and long-term stabilisers to impart heat stability during the life-time of the polyethylene product.

Thus a package of several stabilisers will be used in the polyethylene, at levels typically between 0.05% and 0.2%. Some unstabilised *Alkathene* LDPE grades can be used in several applications (e.g. injection moulding, extrusion coating) but many grades are formulated with a small amount of stabiliser; all *Alkatuff*, *Alkamax*, *Alkatane* and *Alkadyne* grades on the other hand contain a level of stabilisation.

Excessive use of stabilisers is not recommended as this may have adverse effects, such as blooming to the surface, inhibition of surface oxidation where adhesion is required (in extrusion coating), or interference with the corona treatment and printability of films.

There are two basic types of antioxidant, viz. primary and secondary antioxidants. The majority of the **primary antioxidants** for polyethylene are sterically-hindered phenols and these act by reacting rapidly with peroxy radicals generated in the polymer by the action of heat and oxygen. These antioxidants provide excellent processing stability and are most important for the long-term heat stabilisation of polyethylene.

Secondary antioxidants act as synergists in combination with the primary (phenolic) antioxidant. Phosphite and phosphonite-type secondary antioxidants are most effective in providing superior processing stability, but do not contribute to long-term heat stability. They react with hydroperoxides formed during the oxidation process to yield non-reactive products. Thioester antioxidants do not contribute significantly to processing stability but improve long-term heat stability performance in combination with the phenolic antioxidants.

It should be noted that special stabiliser packages may be required for high temperature processes such as cast film extrusion or rotational moulding. In addition, *Alkathene* LDPE and *Alkatuff* LLDPE polymers used in contact with copper, e.g. for telecommunication wire insulation, should also contain a metal deactivator in the stabiliser package for maximum long-term stability. The use of fillers in polyethylene may have a negative effect on the stability of the polymer and so special additive systems will be required.

Evaluation of Oxidative Stability

Processing stability is generally determined by the multi-pass extrusion test in which the changes in MFI and colour of the extrudate are measured after a number of passes of the polyethylene through an extruder. In well stabilised polyethylene, only a small decrease in MFI will be observed after five or nine passes compared with a much larger decrease for poorly stabilised polyethylene.

Long-term heat stability is mostly determined in oven ageing tests at elevated temperatures (e.g. 80 to 120°C), in order to accelerate the effects of oxidation. Results are extrapolated to ambient (or use) temperature to estimate the expected useful life. (However, these extrapolations should be viewed with some scepticism, as different oxidation mechanisms may occur at the elevated temperature compared with ambient temperature).

The criterion of failure can be brittleness, discolouration or loss in tensile properties (particularly tensile elongation).

The effectiveness of various antioxidants in a polyethylene can be assessed by measuring the oxidation induction time at a chosen temperature using the DSC (see Figure 22).

Resistance to Weathering (Ultra-Violet Degradation)

Long-term outdoor exposure of polyethylene to ultraviolet (UV) light at ambient temperature causes photo oxidation of the polymer. UV light is a component of the light spectrum and polyethylene is particularly sensitive to UV light of wavelengths from about 300 to 400 nanometres. This component is most damaging as it has sufficient energy to break carbon-carbon bonds.

The UV light is absorbed by photo-unstable impurities in the polyethylene, sensitising the polymer and initiating the photochemical degradation reactions.

The oxidation begins superficially, causing surface crazing and a marked deterioration of mechanical properties at the surface, but with prolonged exposure the whole of the material becomes degraded, the most obvious effect being that the sample becomes very brittle. The oxidation may be followed by measuring the increase in dielectric loss angle or the reduction in tensile elongation at break. In film, the increase in carbonyl groups may be measured by infra-red spectroscopy.

Use of Carbon Black

Antioxidants that are commonly incorporated as protection against thermal oxidation are not very effective against photo-oxidation. Long-lasting protection can be achieved, however, by incorporation of 2 to 3% of carbon black which absorbs the damaging UV light and restricts its activity to the surface.

Carbon blacks of particle size 10 to 25 nanometres have been found most effective, but they must be uniformly and well dispersed so that no aggregates remain. The degree of mixing normally obtained in extrusion or moulding machines is often insufficient to obtain adequate dispersion when using black masterbatches or carbon black pigment in a natural polymer. For this reason, melt-compounded grades of polyethylene containing about 2.5% carbon black are supplied.

Although carbon black alone is a reasonably effective antioxidant, organic antioxidants are commonly added to give further protection, particularly against the effects of high temperatures which may be attained in black compounds when exposed to sunlight.

Use of Ultra-Violet Stabilisers

When protection against UV degradation is required in natural or pigmented products, the usual practice is to use a small percentage of an organic ultra-violet stabiliser. These may be one of three different types, viz., ultra-violet light absorbers which preferentially absorb the incident UV radiation, thereby screening this radiation from the polymer; ultra-violet quenchers, which deactivate or quench parts of the polymer molecule that have been activated by the UV light; and hindered amine light stabilisers (HALS), which act by inhibiting degradation of the polymer through free-radical scavenging reactions.

Often two different additives will be used in combination in order to impart maximum weather resistance. These additives are used at levels between 0.1 and 1.0%, the level depending on the required lifetime, the sample thickness, and the expected exposure conditions.

Typical Useful Life

Unprotected polyethylene is not recommended for extended outdoor exposure, being suitable only for a very limited term of outdoor use. With the use of UV stabilisers, the life of exposed samples can be extended; such formulations when used in natural films will give a weathering resistance of two to three years. Thick sections of polyethylene suitably protected with about 2.5% of well-dispersed carbon black should remain serviceable under natural weathering conditions for at least 15 years in the tropics, and over 20 years in temperate climates; thinner films will have shorter lifetimes than this.

Because of the great variety of weather conditions in Australia both geographically and between summer and winter, and the influence of product design, thickness and fabrication conditions, no blanket statement can be made as to the serviceable life of any polyethylene formulation, and any information given should only be used as a guideline to the expected performance.

1 GENERAL PROPERTIES

FLAMMABILITY

Combustion of Polyethylenes

Polyethylene, like other organic materials, is combustible and will burn when exposed to adequate amounts of heat and oxygen. Its pyrolysis/combustion behaviour is very similar to that of wood and other cellulosic materials.

When heated in air, polyethylene melts and decomposition will commence at about 300°C. When heated above this temperature polyethylene will pyrolyse oxidatively to produce carbon monoxide and water plus a small amount of various hydrocarbons and aldehydes. The evolved gases can be ignited, and sufficient heat can be generated to accelerate the pyrolysis and allow combustion of more polyethylene or other combustible material in the vicinity. Burning is accompanied by the release of flaming molten droplets of polymer which can ignite adjacent flammable material. Carbonisation also occurs and some of the carbon is released as soot.

The main combustion products are carbon monoxide, carbon dioxide, water and carbon (soot), depending on the temperature and the availability of oxygen. A considerable number of breakdown and oxidation products, normally in very low concentrations, can also be present. These can include aldehydes such as formaldehyde and acrolein. Under normal plant running conditions, atmosphere analyses have indicated that the concentrations of these gases adjacent to an extrusion die are below the Threshold Limit Values recommended for safe working.

The self-ignition temperature for polyethylene, as measured by ASTM D1929, is 350°C. This is a small scale test and its relevance to a real situation is uncertain, but the temperature result is indicative of the effect that may occur by leaving polyethylene in air at these temperatures.

Flame Retardants

With the need to impart flame resistance to plastics for use in the building, transportation, furniture and clothing industries, a range of flame retardant chemicals has been developed. These include: antimony trioxide, chlorine and bromine-containing compounds, aluminium trihydrate and compounds based on phosphorus and boron.

Antimony trioxide in conjunction with a source of halogen gas (e.g. chlorinated or brominated paraffin) is an effective flame retardant system. This system is generally not preferred because of the toxicity of the antimony. There has been a trend away from halogen-based flame retardants because of the corrosive atmosphere generated. Aluminium trihydrate, magnesium hydroxide and boron containing compounds have been receiving attention as flame retardants, and are effective in polyethylene. These additive types act by breaking down under heat to release water vapour. Phosphorus-based intumescent systems are also effective, and these form a protective layer of carbon char on the polymer surface.

Flame retardants act by several mechanisms: physically by cooling the polymer, forming a protective coating, or by dilution of the solid and gaseous phases with fillers and inert vapours; and chemically by interfering with the combustion reactions in the solid and gaseous phases.

Flammability Tests

A number of tests have been developed to evaluate the burning characteristics of thermoplastics. The Limiting Oxygen Index (LOI) test (ASTM D2863) determines the minimum oxygen concentration in an oxygen/nitrogen mixture which just supports burning of the material under specified test conditions; this test is used mainly as a screening test. In the Underwriters Laboratories UL94 vertical flammability test, the material is rated according to a number of criteria relating to its performance after removal of a flame and the degree of dripping.

Polyethylene has an LOI of 17 and a UL94 V-2 (poor) rating. With the addition of suitable flame retardants, an LOI up to about 28 and a UL94 V-0 (good) rating can be achieved.

It is often found that the smoke evolution from burning plastics is the most serious hazard. Smoke emission and smoke density can be determined by the National Bureau of Standards (NBS) smoke chamber test, which measures the obscuring of visible light by smoke generated by the burning sample. Smoke suppressants are sometimes used to avoid this problem.

PERMEABILITY

A key requirement in many polyethylene packaging applications is for the polyethylene to provide a barrier against the transmission of various gases, vapours and liquids. Transmission occurs through the non-crystalline regions of the polyethylene and consequently those polymers with higher crystallinity, i.e., higher density, will provide the better barrier properties and the lower permeability. The permeability of polyethylene approximately halves as the density is increased from 0.920 to 0.940 g/cm³. Permeability is almost independent of MFI.

The permeation or transmission rate of gases and water vapour through polyethylene is dependent on thickness, the conditions of use, and the polarity and molecular weight of the permeating gas or liquid. Lower transmission rates are obtained with thicker wall sections and at lower temperatures.

Polyethylene is an excellent barrier to most liquids, although there are some organic chemicals such as ethers, hydrocarbons and chlorinated hydrocarbons which permeate through polyethylene film very rapidly. In addition, some essential oils diffuse through film and evaporate from the outer surface. The transmission rates for a number of organic liquids and oils through polyethylene of density 0.920 g/cm³ are given in Table 17.

Table 17: Transmission Rate of Polyethylene to Some Liquids at 20°C (density 0.920 g/cm³)

Liquid	Transmission Rate*
Dibutyl ether	3.10
Diethyl ether	6.35
Ethyl bromide	10.5
Chloroform	11.2
Lemon oil	110
Orange oil	108
Grapefruit oil	129

* Thickness 25 microns

The permeability of polyethylene to water vapour is very low; however the transmission rate is very dependent on both temperature and relative humidity, as is illustrated for a 25 micron Alkathene LDPE film grade (MFI 7, density 0.918 g/cm³) in Figure 23.

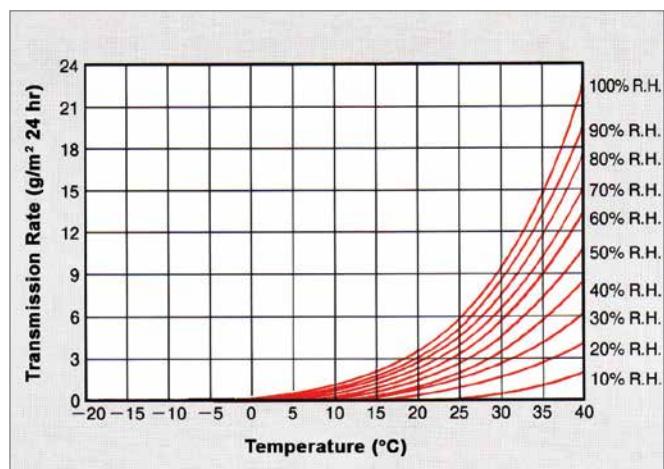


Figure 23: Water Vapour Transmission Rate of 25 micron Polyethylene Film (MFI 7, density 0.918 g/cm³)

Typical transmission rates of various gases through polyethylene film compared with those through a number of other polymer films commonly used in packaging applications are shown in Table 18.

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Table 18: Relative Gas and Water Vapour Transmission Rates of Polyethylene and Other Packaging Films

Film	Gas Transmission Rate (for 25 micron film at 20°C, 1 atm). (cm³/m², 24hr)			Water Vapour Transmission Rate (for 25 micron film at 38°C, 90% R.H.) (g/m², 24 hr)
	O₂	N₂	CO₂	
Polyethylene LDPE (0.920 g/cm³)	8500	3000	38000	18
Polyethylene HDPE (0.960 g/cm³)	3000	650	9000	8
Ethylene Vinyl Acetate EVA Copolymer (18% VA)	12000	6200	45000	70
Ionomer	6500	—	6500	30
Polypropylene Biaxially oriented (BOPP)	1900	500	5500	6
Polypropylene PVdC coated BOPP	16	4	30	6
Polypropylene, cast	4200	750	10000	12
Polystyrene	3500	1000	17000	130
Cellulose Acetate	2500	—	16000	200
Regenerated cellulose*	660	—	1000	10
Polyvinylchloride, Plasticised PVC*	2000+	—	15000	27
Polyvinylchloride, Rigid PVC	250	—	750	50
Polyethylene Terephthalate PET	60	15	250	25
PA barrier resin	30	—	475	—
Polyvinylidene Chloride PVDC	15	3	50	3.5
Ethylene Vinyl Alcohol* (EVOH)	1.8	0.15	7	—

*Moisture dependent

The many sets of units used for the gas permeability of polymer films is a source of frequent confusion, and lists are available for converting from one set of units to another. Extra confusion arises when the data relates to different thicknesses and humidity/temperature conditions.

The data listed in Table 18 are for the Transmission Rates through 25 micron film at 20°C for a 1 atmosphere pressure differential. They can be corrected to other thicknesses by multiplying by: 25/(new thickness in microns), provided the new thickness is within the range of 10 to 200 microns and the pressure differential is still one atmosphere.

For gas transmission through films, the transmission rate as listed in Table 15 has the dimensions:

[Volume/(Area x Time)]

Other conventions use the 'Permeability' or the 'Permeability Coefficient'.

The Permeability has the dimensions:

[Volume/(Area x Time x Pressure Differential)]

Provided the pressure differential is one atmosphere, values for the Permeability are identical with the Gas Transmission Rates as listed above.

The Permeability Coefficient has the dimensions:

[Volume x Thickness/(Area x Time x Pressure Differential)]

and the unit adopted for this parameter by the ASTM is the barrier, which is:

ml(at STP), cm / cm², sec, cm Hg x 10¹⁰

The Permeability Coefficient is the Permeability multiplied by the thickness and, within limits, is independent of thickness. The above Gas Transmission data can be approximately converted into barrers by multiplying by 3.8×10^{-4} .

APPROVAL FOR USE IN CONTACT WITH FOODSTUFFS

In general, most Qenos polyethylene grades are widely approved for use in contact with foodstuffs, and these grades comply with the requirements of the US Food & Drug Administration (F&DA) and of Australian Standard AS2070 Part 1: "Plastics Materials for Food Contact Use". Some grades, however, contain certain additives with restricted approval. If polyethylene is used for food contact applications, then the user needs to ensure compliance with the requirements of the relevant regulations.

For further information, please to the Qenos website or contact your primary Qenos representative.

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APPENDIX 1: MANUFACTURE OF POLYETHYLENE

High Pressure Processes

Low density branched polyethylene (LDPE) is produced by the high pressure free-radical polymerisation of ethylene. Pressures are between 100 to 200 MPa and temperatures are between 150 and 300°C. The polymerisation is carried out in either a stirred-autoclave reactor or a tubular reactor. A flow diagram for the process is shown in Figure 24.

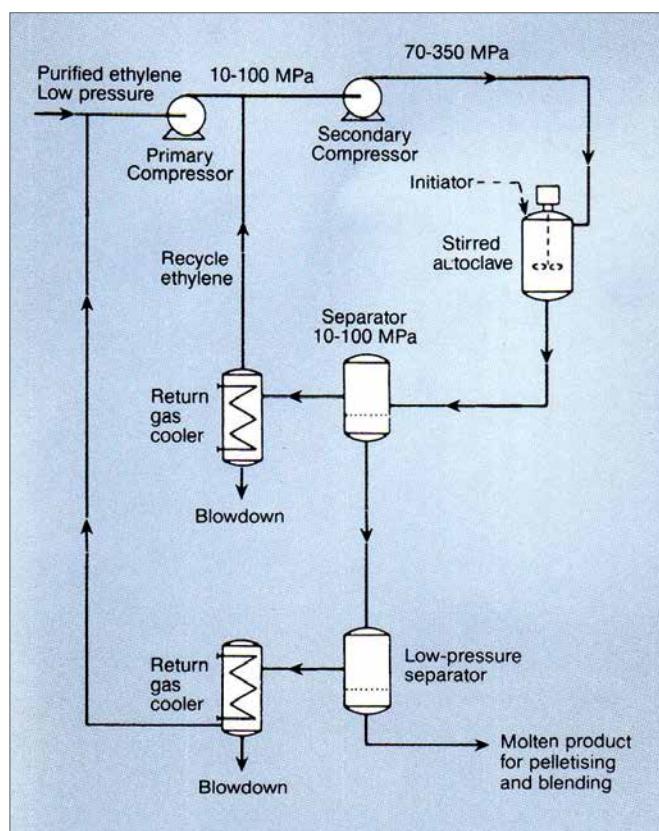


Figure 24: Simplified Flow Sheet for High Pressure Polymerisation of Low Density Polyethylene (LDPE)

The polymerisation reaction involves free-radical initiation, polymer chain propagation, and radical recombination and chain transfer. The polymerisation is initiated either by oxygen, or several, free-radical-producing compounds such as peroxides. The molecular weight is determined by chain transfer either using hydrogen or an alkane as the chain transfer agent. Short chain branches, mainly ethyl and butyl groups, are produced by intra-molecular chain transfer via a “back-biting” reaction. Long chain branches are produced by inter-molecular transfer between a completed polymer molecule and a growing polymer radical.

The process as represented in Figure 24 starts with the two-stage compression of purified ethylene to between 100 and 200 MPa. The high pressure ethylene with initiator and chain transfer agent are fed to the reactor where polymerisation occurs. Because of the highly exothermic reaction, heat must be removed through the reactor walls to avoid any decomposition. Following the polymerisation reaction, where the conversion can be 15 to 25%, unreacted ethylene is separated from the polymer for recirculation and the molten polymer goes to a pelletisation stage.

In the stirred-autoclave process, residence times may be between 30 seconds and 2 minutes. The reaction may be carried out in a zoned reactor to modify the molecular structure of the polymer.

In the tubular process, the reactor is a high pressure tube with a diameter ranging from 2.5 to 6.5 cm and a length of 0.5 to 1.5 km. Residence times are between 20 seconds and 2 minutes.

Genos produces *Alkathene* LDPE at its Botany (NSW) plant by the high pressure stirred-autoclave process.

Low Pressure Processes

Low pressure processes for the polymerisation of ethylene developed from the work of Ziegler and Natta on transition-metal catalysts. These processes operate at pressures of less than 10 MPa, and characteristically produce a linear high density polyethylene (HDPE) in contrast to the highly branched structures obtained in high pressure processes. Lower density linear polyethylene (LLDPE) is obtained by using special transition-metal catalysts and copolymerising the ethylene with alpha-olefin comonomers such as butene-1, hexene-1, octene-1 or 4-methyl-pentene-1.

The polymer molecule grows by insertion of ethylene at the interface between the polymer and the transition-metal catalyst. Hydrogen is used for chain termination to control molecular weight. No long chain branching reactions occur and short chain branches are achieved by copolymerising the ethylene with alpha-olefin comonomers such as butene-1, hexene-1, octene-1 or 4-methyl-pentene-1.

Several different low pressure processes have been developed:

- Solution-phase processes, in which polymerisation takes place in a hydrocarbon solvent (e.g. cyclohexane) above the melting point of the polymer. Typical reaction conditions are 250°C and 8 MPa. The polymer is recovered by evaporating the solvent and unreacted monomer for recycling.
- Modified high pressure processes, where linear polyethylene can be produced in a high pressure reactor by using organo-metallic catalysts.
- Slurry-phase processes, where the polymerisation takes place at a temperature below the melting point of the polymer in a liquid diluent in which the polymer is

essentially insoluble. The polymer forms as suspended particles. In the slurry stirred-reactor process, the diluent is hexane or heptane, the polymerisation conditions 70 to 90°C and less than 1 MPa pressure, and the catalyst a titanium halide-aluminium alkyl type catalyst. This process is used by Qenos to produce some HDPE grades used in blow moulding, pipe and film applications. In the process, isobutane is used as the diluent and the catalyst is a supported chromium oxide; typical polymerisation conditions are 90 to 150°C and 2 to 4 MPa pressure (see Figure 25).

Qenos produces a range of *Alkatane* and *Alkadyne* HDPE grades at its Resins Altona plant using the Slurry Phase Process.

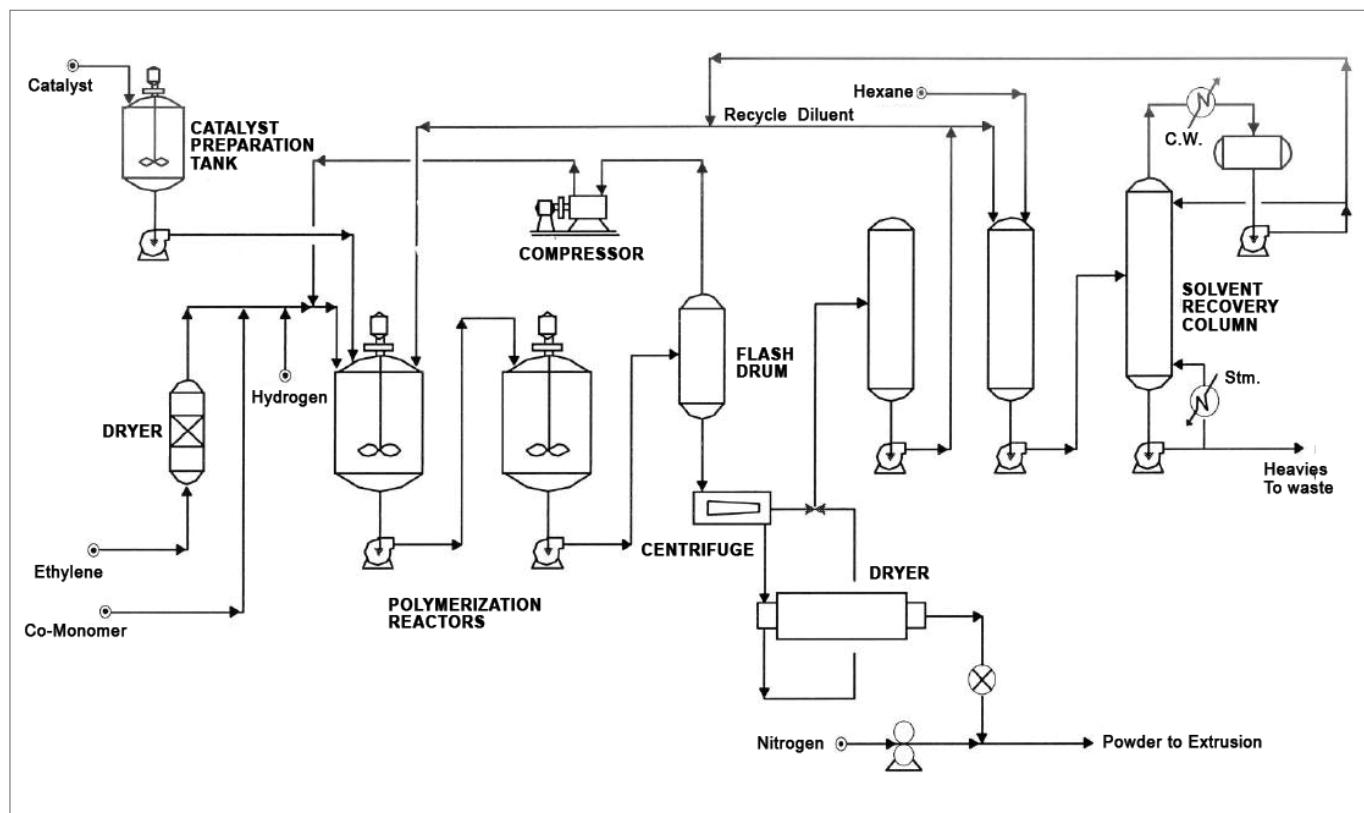


Figure 25: Simplified Flow Sheet of the Slurry Phase Process for Producing HDPE

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- d. Gas-phase processes, in which gaseous ethylene is polymerised on or within particles of polyethylene. Reaction conditions are typically below 100°C and 2 to 3 MPa. The gas-phase polymerisation technology that utilises a fluidised-bed process, is shown schematically in Figure 26. Solid polyethylene is removed from the reactor through differential pressure valves and passes to the pelletising plant.

Qenos produces *Alkatuff LLDPE* and *Alkamax mLLDPE* at its Botany (NSW) plant by the fluidised-bed process licensed from Univation.

Qenos produces a range of *Alkatane* and *Alkadyne HDPE* grades at its Plastics Altona plant by the fluidised-bed process licensed from Univation.

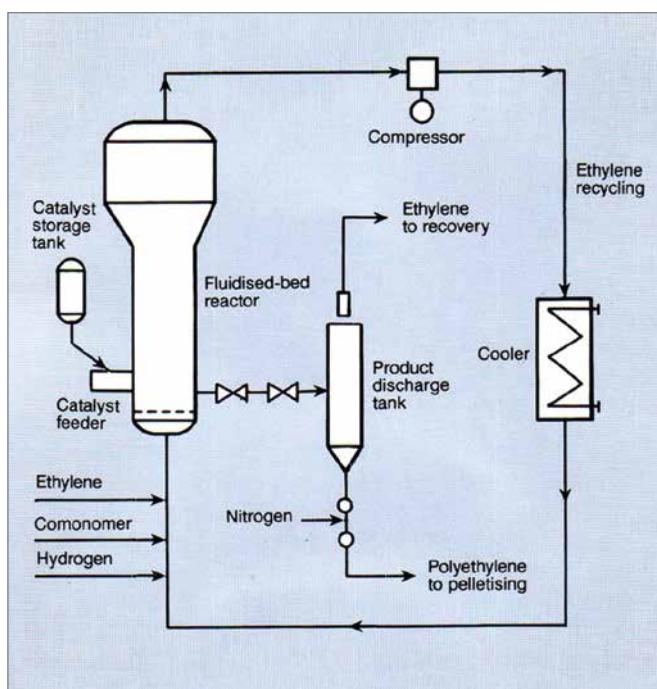


Figure 26: Simplified flow Sheet of the Gas-phase Fluidised-bed Process for Producing LLDPE/HDPE

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