

5.1. Polyethylene

5.1.1. Introduction

Despite ethylene's simple structure, the field of polyethylene is a complex one with a very wide range of types and many different manufacturing processes. From a comparatively late start, polyethylene production has increased rapidly to make polyethylene the major tonnage plastics material worldwide (45×10^6 t capacity in 1995). In the 1920s research into the polymerization of unsaturated compounds such as vinyl chloride, vinyl acetate, and styrene led to industrial processes being introduced in the 1930s, but the use of the same techniques with ethylene did not lead to high polymers. The chance observation in 1933 by an ICI research team that traces of a waxy polymer were formed when ethylene and benzaldehyde were subjected to a temperature of 170°C and a pressure of 190 MPa, led to the first patent in 1936 and small-scale production in 1939. The polymers made in this way, by using free radical initiators, were partially crystalline, and measurement of the density of the product was quickly established as a means of determining the crystallinity. Due to the side reactions occurring at the high temperatures employed, the polymer chains were branched, and densities of $915\text{--}925\text{ kg/m}^3$ were typically obtained. The densities of completely amorphous and completely crystalline polyethylene would be 880 and 1000 kg/m^3 , respectively.

During the 1950s three research groups working independently discovered three different catalysts which allowed the production of essentially linear polyethylene at low pressure and temperature. These polymers had densities in the region of 960 kg/m^3 , and became known as high-density polyethylenes (HDPE), in contrast to the polymers produced by the extensively commercialized high-pressure process, which were named low-density polyethylenes (LDPE). These discoveries laid the basis for the coordination catalysis of ethylene polymerization, which has continued to diversify. Of the three discoveries at Standard Oil (Indiana), Phillips Petroleum, and by KARL ZIEGLER at the Max-Planck-Institut für Kohlenforschung, the latter two have been extensively commercialized. More recently the observation that traces of water can dramatically increase the polymerization rate of certain Ziegler catalysts has led to major developments in soluble coordination catalysts and later their supported variants.

The coordination catalysts allowed for the first time the copolymerization of ethylene with other olefins such as butene, which by introducing side branches reduces the crystallinity and allows a low-density polyethylene to be produced at comparatively low pressures. Although DuPont of Canada introduced such a process in 1960, worldwide the products remained a small-volume specialty until 1978 when Union Carbide announced their Unipol process and coined the name linear low-density polyethylene (LLDPE). In addition to developing a cheaper production process, Union Carbide introduced the concept of exploiting the different molecular structure of the linear

Table 1. Polyethylene production capacities in 10^3 t/a * (1995)

	North America	Western Europe	Eastern Europe	Japan	Rest of World	Total
LDPE	3891	5783	1918	1444	4210	17 246
LLDPE	4422	1848	100	1059	3728	11 157
HDPE	6198	4008	873	1024	4715	16 891
Total PE	14 511	11 639	2891	3527	12 653	45 221

* Data from Chem Systems, London.

product to make tougher film. Following this lead, LLDPE processes have been introduced by many other manufacturers.

The history of these discoveries is covered in [1]–[4], [20].

The three types of polyethylene outlined above account for the major part of polyethylene production (Table 1), but the picture is slightly confused since many plants have the capability of producing more than one type of product (so-called swing plants). Additionally, copolymers are made by both types of process. The free-radical process is used to produce copolymers of vinyl acetate, acrylates, methacrylates, and the corresponding acids, but chain transfer prevents the use of higher olefins because of the drastic reduction in molecular mass of the polymer. The coordination catalysts are able to copolymerize olefins, but are deactivated by more polar materials. Because of the complex interplay of the capabilities of modern plants, it is convenient to treat separately the products, the catalysts, and the processes.

5.1.2. Properties of Polyethylenes

5.1.2.1. Molecular Structure and Morphology

Figure 1 shows schematic structures for the three polyethylenes, with the main features exaggerated for emphasis. LDPE has a random long-branching structure, with branches on branches. The short branches are not uniform in length but are mainly four or two carbon atoms long. The ethyl branches probably occur in pairs [21], and there may be some clustering of other branches [22]. The molecular mass distribution (MMD) is moderately broad.

LLDPE has branching of uniform length which is randomly distributed along a given chain, but there is a spread of average concentrations between chains, the highest concentrations of branches being generally in the shorter chains [23]. The catalysts used to minimize this effect generally also produce fairly narrow MMDs.

HDPE is essentially free of both long and short branching, although very small amounts may be deliberately incorporated to achieve specific product targets. The MMD depends on the catalyst type but is typically of medium width.

Polyethylene crystallizes in the form of platelets (lamellae) with a unit cell similar to that of low molecular mass paraffin waxes [24]. Due to chain folding, the molecular axes

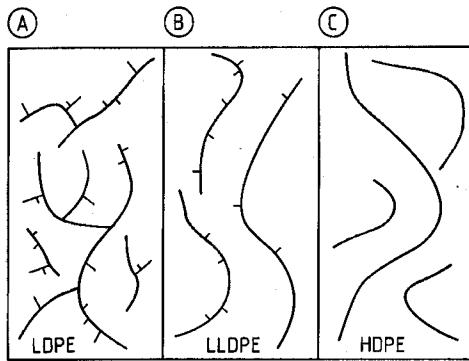


Figure 1. Schematic molecular structure
A) Low-density polyethylene; B) Linear low-density polyethylene; C) High-density polyethylene

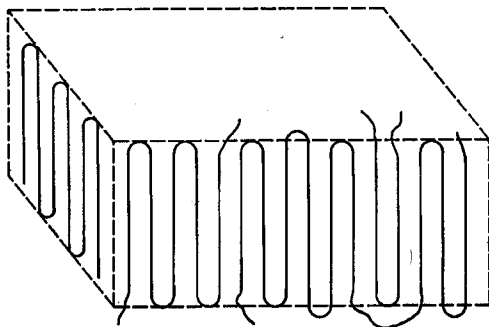


Figure 2. Folded-chain lamellar crystal of polyethylene

are oriented perpendicular to the longest dimension of the lamella and not parallel to it as might be expected (Fig. 2). The thickness of the lamellae is determined by the crystallization conditions and the concentration of branches and is typically in the range of 8–20 nm. Thicker lamellae are associated with higher melting points and higher overall crystallinities. Slow cooling from the melt or annealing just below the melting point produces thicker lamellae. Where long molecules emerge from the lamella they may either loop back elsewhere into the same lamella or crystallize in one or more adjacent lamellae, thereby forming "tie molecules".

Thermodynamically the side branches are excluded from the crystalline region because their geometry is too different from that of the main chains to enter the crystalline lamellae. Therefore, the branches initiate chain folding, which results in thinner lamellae with the branches mainly situated on the chain folds on the surface of the lamellae. However, on rapid cooling these energetically preferred placements may not always occur, and some branches may become incorporated as crystal defects in the crystalline regions. Detailed measurements by solid-state NMR and Raman spectroscopy show that the categorization into crystalline and amorphous phases is too simplistic and a significant fraction of the polymer is present in the form of an "interfacial" fraction which has neither the freedom of motion of a liquid, nor the well-defined order of a crystal [25], [26]. A further result of a side branch is that having been prevented

from folding directly into the same lamella, the polymer chain may form a tie molecule that links to one or more further lamellae.

Under moderately slow cooling conditions, crystallization may be nucleated at a comparatively small number of sites. Crystallization then propagates outwards from these centers until the surfaces of the growing spheres meet. The resulting spherulites show a characteristic banded structure under a polarizing optical microscope. The typical milkiness of polyethylene is due to light scattered by spherulites or other, less well defined aggregates of crystallites, rather than by the crystallites themselves, which are much smaller than the wavelength of light [27]. Ethylene copolymers may be transparent, although partially crystalline.

5.1.2.2. General Properties

LDPE and LLDPE are translucent whitish solids and are fairly flexible. In the form of films they have a limp feel and are transparent with only a slight milkiness. HDPE on the other hand is a white opaque solid that is more rigid and forms films which have a more turbid appearance and a crisp feel.

Polyethylene does not dissolve in any solvent at room temperature, but dissolves readily in aromatic and chlorinated hydrocarbons above its melting point. On cooling, the solutions tend to form gels which are difficult to filter. Although LDPE and LLDPE do not dissolve at room temperature, they may swell in certain solvents with a deterioration in mechanical strength. Manufacturers issue data sheets detailing the suitability of their products for use in contact with a wide range of materials. In addition to solvents, polyethylene is also susceptible to surface active agents which encourage the formation of cracks in stressed areas over prolonged periods of exposure. This phenomenon, known as environmental stress cracking (ESC), is believed to be due to lowering of the crack propagation energy [28]. In general, HDPE is the preferred polyethylene for liquid containers.

5.1.3. Polymerization Chemistry

Heat of Reaction. The heat of polymerization of ethylene is 93.6 kJ/mol (3.34 kJ/g). Since the specific heat of ethylene is $2.08 \text{ J}^\circ\text{C}^{-1} \text{ g}^{-1}$, the temperature rise in the gas phase is ca. 16 °C for each 1 % conversion to polymer. Heat removal is thus a key factor in a commercial polymerization process. Some processes (e.g., ICI autoclave, Unipol fluidized bed) employ only a limited conversion per pass, and the heat of reaction is absorbed by the cool reactants. The unreacted monomer is then cooled in the recycle stage. In other cases (e.g., UCC or BASF tubular and various slurry processes) more surface area or more residence time is provided, and heat is removed through the reactor walls.

5.1.3.1. Free-Radical Catalysis

5.1.3.1.1. Introduction

Free-radical catalysis is used exclusively in the high-pressure process, that is at pressures above 100 MPa. The reason for the use of such high pressures is a combination of historic, economic, and technical factors [39]. Because ethylene is gaseous above its critical temperature of 9 °C, a pressure of ca. 20 MPa would be necessary in any case to achieve a reasonable concentration of monomer. Employing pressures of ca. 200 MPa and temperatures above 160 °C enables the polyethylene produced to dissolve in the unreacted ethylene, and the high reaction rate makes the best use of the very expensive high-pressure equipment. 20 % conversion of the monomer is typically achieved in 40 s. A schematic phase diagram for an ethylene–polyethylene system is shown in Figure 10 [48]. For a more detailed account of the effect of molecular mass and MMD on the phase equilibria, see [49].

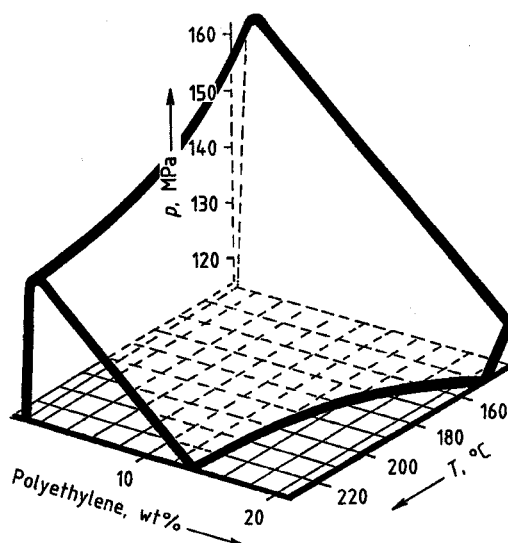


Figure 10. Schematic cloud point surface for ethylene-polyethylene [48]

The single-phase ethylene-polyethylene mixture allows the reaction to take place as a classical free-radical-initiated solution polymerization. Some aspects which are particularly important for ethylene systems are as follows:

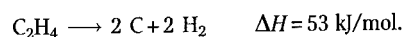
- 1) In addition to the effect of concentrating the gaseous monomer, the pressure also influences the reaction rate constants, as is also the case for liquid systems subjected to high pressures [50]. This is generally considered in terms of a volume of activation, analogous to the energy of activation. High pressure affects the configuration change necessary for the reactants to reach the transition state. The overall contribution of the effect of pressure on the rate constants over the pressure range 0 to 200 MPa is to increase the polymerization rate by a factor of ca. 12 [51].
- 2) The reaction temperatures employed are also high, an average of ca. 220 °C being typical. In parts of the reactor the temperature may be as low as 140 °C but in other parts may reach over 300 °C. These high temperatures also contribute to the high reaction rates, the activation energy being 32 kJ/mol.
- 3) The growing polymer chains are linear alkyl radicals and as such are very reactive not merely in the addition to double bonds, but also in abstracting hydrogen atoms from other molecules, thereby forming saturated alkyl chains and new radicals. The process is called chain transfer. Since these hydrogen atom abstraction reactions have higher activation energies than polymerization, they become increasingly important as the polymerization temperature rises. On the one hand they put stringent demands on the monomer purity to avoid traces of compounds which could give rise to chain transfer and thereby reduce the molecular mass, and on the other hand it is possible to use low concentrations of suitable materials (so-called chain-transfer agents or modifiers) to control the polymer molecular mass. Chain-transfer agents which have been used commercially include hydrogen, propane,

propene, acetone, and methyl ethyl ketone. Chain transfer to some compounds with very active hydrogen atoms such as propene, and particularly the higher alkenes, can lead to radicals which are insufficiently reactive towards ethylene to reinitiate new chains rapidly, and reduced reaction rates result.

- 4) Chain transfer can also occur with the polyethylene chains themselves, either to the same growing chain (intramolecular) or to other polyethylene chains (intermolecular transfer). These reactions create the characteristic structural features of LDPE which distinguish it from HDPE. As can be demonstrated with models, the most probable intramolecular chain-transfer reaction is to the carbon atom four carbons back down the chain, which produces butyl groups (Fig. 11 A). This so-called back-biting mechanism was first published by M. J. ROEDEL of DuPont [52]. If, after the addition of one ethylene molecule to the newly formed secondary radical, a further back-bite occurs (Fig. 11 B), a pair of ethyl branches or a 2-ethylhexyl group is formed. A further possibility, shown in Figure 11 C, is that a back-bite occurs to a branch point, and the tertiary radical then decomposes into a new short radical, leaving a vinylidene group at the end of the polyethylene chain. This process is the principal chain-termination mechanism in LDPE, and concentrations of vinylidene groups approach one per number average molecule for LDPEs produced at high temperature. These three reactions account for the principal features observed in the infrared spectrum of LDPE, but to a lesser extent other intramolecular transfers also occur [9]. Since the activation energy for transfer is higher than for the polymerization reaction and the activation volume is smaller, branching and unsaturation increase with increasing polymerization temperature and decrease with increasing reaction pressure [53], [54].
- 5) Intermolecular transfer leads to long branching and broadening of the molecular mass distribution. Since they have more hydrogen atoms available for chain transfer, the long chains tend to be the most highly branched, and there may be branches on the branches. Statistically each new radical produced by initiation or chain-transfer reactions has a range of probabilities of growing to various lengths before being terminated by one of these same chain-transfer or radical combination reactions. The probable length is the same whether the chain grows from a new initiating radical or a branch point. Thus branches are statistically the same length as the backbone itself and, taking into account statistical variations, the branches may in some cases be longer than the initial backbone. Since the long-branching reaction is a chain-transfer mechanism, the average chain length of an unbranched molecule or a branch is shorter than it would be in the absence of the long-branching reaction. The effects of temperature and pressure are similar to those for short branching, but additionally the amount of long branching is proportional to the concentration of dissolved polymer. In principle, this leads to a clear difference between plug flow (tubular) and continuous stirred-tank reactors (CSTRs, autoclaves). Theoretical analyses have been presented for autoclave [55], [56], [57] and tubular [58] reactors.
- 6) Initiation is very similar to that in many other free-radical polymerizations, but there are some limitations. Initiators are commonly referred to as "catalysts". In the

sense that one mole of initiator will achieve the polymerization of several thousand moles of ethylene this is so, but the initiator is destroyed in the process and so the term is, strictly speaking, incorrect. Oxygen was used as initiator in the early commercial processes because of the ease of introducing it into the process. With the development of high-pressure pumps and new initiators, modern plants are able to maintain more precise control of temperature profiles by the injection of solutions of liquid catalysts. The mechanism by which oxygen forms free radicals is rather complicated, and at lower temperatures oxygen can act as an inhibitor [59]. In the autoclave process the use of oxygen has been largely superseded, but in the tubular reactor process it is still widely used, sometimes in combination with liquid initiators. The two overall limitations on initiators are that they should be readily soluble in alkanes and they should produce reactive radicals, ideally alkyl or alkoxy radicals. On the former count, all the aqueous systems and most azo compounds are excluded, and on the second count dibenzoyl peroxide is unsuitable. The initiators are selected for use on the basis of their half-lives at the reaction temperature. Since the residence time in the reactor zone may be of the order of 20 s or less, to obtain good control of the reaction rate, an initiator half-life of about 1 s is required. For a tubular reactor the same initiator is active over a wider range of temperatures, but its selection is equally critical. Typical initiators are listed in Table 6 [60].

- 7) The mechanism of kinetic chain termination is by combination of radicals. This further widens the MMD in long-branched systems when the rate of initiation-combination is high [57].
- 8) Although the conversion of ethylene to polyethylene is thermodynamically favorable, the decomposition into carbon and a mixture of methane and hydrogen is also highly exothermic:



For kinetic reasons these reactions are only important at the high temperature and pressures of the high-pressure process. In a confined system the large amount of heat released can raise the temperature, and hence the pressure, of the methane and hydrogen to potentially dangerous levels. The theoretical final temperature and pressure for a contained decomposition starting at 250 °C and 200 MPa are 1400 °C and 620 MPa. In practice much of the heat would be absorbed by the walls of the vessel or pipework. High-pressure plants are designed with relief valves or bursting disks to protect the equipment from overpressurization due to decomposition. Decompositions usually start as a runaway polymerization reaction, but then they can propagate as a slow flame front even into cold gas. Experimental decompositions usually show low propagation velocities of ca. 0.2 m/s [61], but under the more turbulent conditions of commercial plant operation, propagation can be more rapid.

5.1.4. Raw Materials

5.1.4.1. Ethylene

The first polyethylene plant built by ICI used ethylene produced by dehydration of ethanol. Modern ethylene production plants are based on the thermal cracking of hydrocarbon feedstocks at ca. 850 °C. Due to the availability of raw materials, the feedstock used predominantly in North America was originally ethane, with naphtha being used more commonly in Europe. The tendency now is for crackers to be designed to accept a wider range of feedstocks, so as to match the range of coproducts such as propene to the market requirements.

Modern plants produce ethylene with a quality which in many cases is suitable for polymerization with little or no further purification. In North America and Europe, producers supply ethylene to an agreed specification via a common ethylene grid, and polymerization plants take their supplies from these pipelines. In the case of sensitive catalyst systems such as the Phillips catalyst some further purification may be necessary to ensure that maximum impurity levels are not exceeded. Table 8 lists specifications for a polymerization-grade ethylene suitable for most processes. There are overall limits on inert materials such as ethane or nitrogen which, because of the efficient recycle system, could build up and dilute the process stream. The main impurities of importance to the free-radical process are oxygen and water. The former could cause inhibition of low-temperature initiators, or uncontrolled initiation of reaction at higher temperatures. At moderate concentrations (after concentration by the recycle) water can form ethylene hydrate [98] in the cooler parts of the high-pressure process, completely blocking the pipework. Some of the other specified compounds can produce problems of molecular

5.1.6. Uses

Table 11 shows an analysis by end-use of approximately half of the world market for polyethylenes. The pattern is very different for the two classes. LDPE (together with LLDPE which is sold into the same market) is used predominantly for films, not all of which is for packaging. Because of its greater rigidity and better creep properties, HDPE is used in more structural applications, and also has important applications in the packaging of aggressive liquids such as bleach, detergent, and hydrocarbons.

5.1.6.1. Film

LDPE retains its position as a preferred packaging material because of its limp feel, transparency, toughness, and the ability to rapidly take up the shape of the contents of the bag. Other materials such as thinner HDPE film or paper may in some cases be more economical, but are less acceptable to the customer. Most LDPE film is produced by the film blowing process but flat film extruded onto chilled rolls is also made, particularly in the United States. An LDPE for high-clarity film typically has a MFI of 2 and a density of 920 kg/m^3 and is extruded at $160\text{--}180^\circ\text{C}$. The cast film process is usually used with higher density polyethylenes ($930\text{--}935 \text{ kg/m}^3$), where the quenching on the chilled rolls enables good optical properties to be achieved with a higher film stiffness. The bubble diameter in the tubular film process may be up to 2 m for general purpose packaging, and larger for heavy gauge industrial film. Originally, bags were made directly from tubular film by welding one end, but the tendency now is to make wide film on large machines and fabricate the bags by welding and cutting. Apart from packaging film and heavy duty sacks, increasing quantities of polyethylene are used for impermeable or stabilizing membranes in civil engineering construction.

Additives play a particularly important role in the production of LDPE film by the film blowing process. Without additives, the pressure of the windup rollers on the

warm film forces the surfaces into such close contact that subsequently it may be virtually impossible to separate them. High-gloss films are the worst affected. This is overcome by adding an antiblocking agent such as very fine silica, which roughens the surface on a submicroscopic scale without significantly affecting the optical properties. To reduce the friction between the surfaces a slip agent such as oleamide or erucamide is added. Other additives may be added to achieve effects in the final product such as oxidation resistance, UV resistance, or antistatic properties.

A film extruder designed for LDPE requires extensive modifications to allow it to extrude LLDPE at comparable rates [123]–[125]. To avoid this investment and the lack of flexibility, many film manufacturers (particularly in Europe) use blends of LDPE and LLDPE. The equipment modifications required are:

- 1) The screw must have greater clearance between the flights and the barrel to avoid temperature buildup due to the higher shear viscosity. Ideally the screw should be shorter.
- 2) The die gap must be widened to reduce the shear rate and so avoid a type of surface defect, known as shark skin, to which narrow MMD polymers are prone. To some extent this problem can be avoided by incorporating additives based on fluoroelastomers (DuPont, 3M) or silicones (UCC) [126]–[128].
- 3) The cooling ring must give more rapid quenching of the melt to avoid the development of excessive crystalline haze, and also to give more support to the bubble because of the lower tensile viscosity under the inflation conditions. Apart from this lack of inherent stability of the bubble, the low tensile viscosity is responsible for the major product advantage of LLDPE, since high stresses do not occur when the melt is drawn down to thin film. LLDPE can be drawn down to much thinner film without the bubble tearing than can a LDPE with equivalent mechanical properties.

HDPE film is generally made on units specifically optimized for the high molecular mass grades normally used. To produce tough films a balanced orientation of the film is necessary, and a high ratio of die diameter to bubble diameter (“blow ratio”) is used so as to balance the machine direction draw with a high transverse draw. A characteristic stalk-shaped bubble is used in which substantial machine-direction draw takes place before a rapid expansion occurs some distance above the die. Mechanical guides are needed to stabilize the bubble. HDPE film is opaque and is usually used in much thinner gauges than LDPE. It competes with LDPE in areas such as carrier bags and supermarket convenience bags.

5.1.6.2. Extrusion Coating

LDPE is used extensively for coating cardboard, paper, and aluminum for milk cartons etc., for which a very low level of impurities is required. Extrusion is carried out at ca. 300 °C through a wide-slit die. Polymers with a high die swell due to long branching perform best, since the tendency to expand on leaving the die opposes the

“neck-in” tendency when the melt is drawn onto the substrate. A typical LDPE used for this application has a MFI of 4 and a density of 920 kg/m^3 .

5.1.6.3. Blow Molding

HDPE is now the preferred material for blow-molded containers for liquids, combining adequate environmental stress crack resistance with higher rigidity than LDPE, and hence permitting lower bottle weights for a given duty. The major uses are in the domestic market for bleach, detergents, and milk. For this application a HDPE with a MFI of 0.2 and a density of 950 g/m^3 is suitable. Other uses include a variety of industrial containers and gasoline tanks. There is a trend to higher molecular mass and to broader MMD polymers, with bimodal MMDs achieved by using catalyst or reactor developments [129].

5.1.6.4. Injection Molding

Injection molding is used for a variety of products. Some, such as caps and lids are used in the packaging field. Other applications such as housewares, toys, and industrial containers are more durable. According to whether high flexibility is required or not, LDPE or HDPE may be used. Some LLDPEs with a narrow MMD are particularly well suited for this method of fabrication. MFIs range from 2 to > 40 . A narrow MMD gives the best compromise between toughness, flow into the mold, and freedom from warpage in the finished product.

5.1.6.5. Pipe

The use of polyethylene for pipes is one of the few engineering applications, where the applied stresses are carefully assessed and a lifetime of at least 50 years is required. Polyethylene is used for water and natural gas local distribution systems and, unlike many other uses, there is a substantial stress applied continuously. The potential problem is thus long-term stress rupture, and this must be carefully assessed by extrapolation and accelerated testing. Large quantities of pipe made of a medium-density polyethylene designed to withstand a stress in the PE of 8 MPa have been laid, but recent advances in bimodal HDPE polymers now enable a 50-year lifetime at a design stress of 10 MPa to be met. The first polymers which met this specification (PE 100) were introduced by Solvay in their TUB 120 range, but now all major producers have similar polymers in their ranges [130], [36].

5.1.6.6. Wire and Cable Insulation

Because of its outstanding dielectric properties, the first application of polyethylene was the insulation of very high frequency and submarine telephone cables. These have continued to be made from LDPE, but uses have expanded into telephone and power cables. In the latter case cross-linking is increasingly used to enhance the properties and allow a higher current rating for a given size of cable.

5.1.6.7. Ethylene Copolymers

The processing techniques used for copolymers are generally the same as used for polyethylene homopolymers, but the range of applications is generally more diverse [12]. The property most generally exploited is the decreased rigidity to give more flexible film, moldings, and tubing than is possible with LDPE. Copolymers with high comonomer content are generally competitive with plasticized PVC and rubbers, with a low extractable additive content as an advantage. For flexibility down to the lowest temperatures acrylate copolymers are preferred over EVA copolymers. VLDPE copolymers, particularly those made by single-site catalysts, are increasingly being used in applications requiring flexibility combined with thermal stability and good low-temperature flexibility.

Ethylene copolymers are also used in blends, in the same way as rubbers, to confer increased toughness. Particular applications include blends with wax and with bitumen for paper coating and road surfacing, respectively. Copolymers are also used as constituents of hot melt adhesives.