Chapter 4

Detailed accounts of thermoplastic resins

For easier reading, certain elements of earlier chapters are repeated in the opening remarks on each material family and in the sections on 'Applications'. However, for the latter, the reader should refer to Chapter 2 for the most complete and up-to-date information.

Unless otherwise specified, the units used in the property tables at the end of each account are:

Specific mass or density	g/cm^3
Shrinkage	%
Absorption of water	% after 24 h of immersion
Tensile strength	MPa
Elongation at break	%
Tensile modulus	GPa
Flexural strength	MPa
Flexural modulus	GPa
Compression strength	MPa
Notched impact strength ASTM D256	J/m
HDT B (0.46 MPa)	°C
HDT A (1.8 MPa)	°C
Continuous use temperature (unstressed)	°C
Glass transition temperature	°C
Brittle point	°C
Thermal conductivity	W/m.K
Specific heat	cal/g/°C [1 cal = 4.19 J]
Coefficient of thermal expansion	10^{-5}/°C
Volume resistivity	ohm.cm
Loss factor	10^{-4}
Dielectric strength	kV/mm
Arc resistance	s

The data are examples that cannot be generalized and cannot be used for design purposes.

4.1 Polyethylene or polythene (PE)

Albeit having a simple chemical formula, $-(CH_2-CH_2)_n-$, polyethylene is a broad family with versatile properties that depend on which of the three main polymerization processes is used:

- Free radical vinyl polymerization, the oldest process, leads to branched low density polyethylene (LDPE). Macromolecules have numerous short branches, which reduce the melting point, tensile strength and crystallinity. Polymers are relatively flexible because of the high volume of the branched molecule and the low crystallinity.
- Ziegler-Natta polymerization leads to linear unbranched polyethylene, the so-called high density polyethylene (HDPE), which is denser, tougher and more crystalline. By copolymerization with other alkenes it is possible to obtain linear low density polyethylene (LLDPE) with better mechanical properties than LDPE. Blends of LLDPE and LDPE are used to combine the good final mechanical properties of LLDPE and the strength of LDPE in the molten state.
- Metallocene catalysis polymerization is the most recent technique, growing fast to produce a consistent, uniform distribution of molecular weight resulting in enhanced toughness, impact and puncture strengths, better cold behaviour and optical properties. These advantages allow the downgauging or enhancement of performances for the same weight of polymer. Metallocene catalysis allows the production of all densities, from ultra-low density to ultra-high molecular weight polyethylenes (UHMWPE).

In addition to their structural diversity, polyethylenes can be crosslinked.

Polyethylenes can be classified versus density and molecular weight:

- ultra-low and very low density, ULDPE and VLDPE
- low density, LDPE and LLDPE
- medium density, MDPE
- high density, HDPE
- high molecular weight, HMWPE
- ultra-high molecular weight, UHMWPE.

Regardless of molecular weight, polyethylene can be classified into five density categories:

- 0.890 to 0.909 or 0.915
- 0.910 to 0.925
- 0.926 to 0.940
- 0.941 to 0.959
- 0.960 and higher.

Regardless of density, polyethylenes have molecular weights of the order of:

- LDPE & HDPE: from a few thousands to 300 000 depending on the end use
- high molecular weight, HMWPE: approximately 200 000 to 500 000
- ultra-high molecular weight, UHMWPE: approximately 3 000 000 and higher.

Considering the versatility of polyethylenes, each polyethylene subfamily has, of course, its favoured application sectors:

- HDPE is used for 86% of all polyethylene goods having applications that are structural to a greater or lesser degree
- LDPE and LLDPE are used for 86% of all polyethylene films.

Expressed in another way:

- 75% of HDPE is converted into parts having a structural function to a greater or lesser degree
- 75% to 80% of LDPE and LLDPE are converted into films.

For films, Table 4.1 proposes an arbitrary classification of the polyethylene subfamilies (where m indicates metallocene catalysis).

Table 4.1 Films: arbitrary classification of the polyethylene subfamilies

Function	Mechanical	Optical	Organo-leptic	Vapour barrier	Sealability	Processability
mVLDPE	1	1	1	2	1	3
mLLDPE	1	2	1	2	2	3
LLDPE	2	2	2	2	2	3
LDPE	3	2	1	2	2	1
HDPE	3	3	2	1	3	2

1 – generally the best adapted to the function
2 – intermediate behaviour
3 – generally less adapted to the function

The same basic monomer generates a lot of common properties and, unless otherwise specified, we will not make a distinction between the various subfamilies. Only the foams will be given special attention as they present particular properties due to their morphology:

- decreased mechanical properties due to the low quantity of polymer and the high proportion of gas
- weaker chemical resistance due to the highly divided state of the polymer. The thin cell walls immediately absorb liquids and gases.

4.1.1 General properties

Advantages

General advantages are low price, attractive price/property ratios, easy transformation, chemical inertness, impact resistance, low absorption of water, low density (HDPE included), good electrical insulator, low coefficient of friction, suitability for food contact, ease of welding, good machinability for rigid grades; good resistance against high-energy radiation, physiological inertness, versatility of processing methods except for UHMWPE.

- LDPE: good mechanical properties, flexibility, impact resistance at ambient temperature; good insulating material even in a wet medium; chemically inert.
- HDPE: same properties as LDPE but more rigid; better thermal and creep behaviour; lower coefficient of friction and higher pressure strength, allowing antifriction applications with higher PV (pressure*velocity) factor; more transparent.
- UHMWPE: better mechanical properties, lower coefficient of friction and higher pressure strength allowing antifriction applications with higher PV factor.
- Linear PE: same properties as the equivalent branched PE with an improvement in the mechanical properties, thermal and creep behaviour, and resistance to stress cracking.
- Metallocene: enhanced toughness, impact and puncture strengths, better cold behaviour and optical properties.
- Crosslinked PE: more resistant to temperature, creep and cracking.

Drawbacks

General drawbacks are the innate sensitivity to heat, UV, light and weathering (but stabilized grades are marketed), stress cracking, and creep; low rigidity, significant shrinkage, limited transparency. Due to the surface tension, gluing, painting and printing are difficult without surface treatments. Composed only of carbon and hydrogen, polyethylenes are naturally flammable but FR grades are marketed.

Processing is difficult for UHMWPE due to the high molecular weight.

Polyethylene is sensitive to pro-oxidant metals such as copper, manganese or cobalt, which must be avoided as inserts.

Special grades

They can be classified according to the type of processing, specific properties, targeted applications:

- Extrusion, injection, compression, blown film, blow moulding, rotational moulding, foam, coating, powdering, co-extrusion, for thin or thick parts, for crosslinking, electrowelding . . .
- Stabilized against heat, UV, light or weathering; antistatic, conductive, reinforced, food contact, physiologically inert, fireproofed, transparent, resistant to stress cracking, low warpage, high fluidity . . .
- For films, sheets, tubes, wire and cable coatings, fibres, mass production of household requisites, bottle racks, bins, containers, pallets, tubes, prostheses, antifriction parts . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide a rough idea. They are generally of the order of €1 per kilogram.

Processing

All molten-state processing methods are usable: extrusion, injection, compression, blown film, blow moulding, rotational moulding, thermoforming, foam, coating, powdering, co-extrusion, fluidized bed, machining for high hardness grades, welding. Special grades can be crosslinked after shaping.

Applications

(See Chapter 2 for further information.)

Although varying according to country, consumption is approximately divided into:

- 40–45% HDPE
- 30–35% LLDPE
- 20–25% LDPE.

Applications vary according to the polyethylene type.

LDPE and LLDPE are mainly used for:

- films for packaging: food, non-food, shrink, stretch . . .
- films for other applications
- sheets
- extrusion coating
- injection moulding
- blow moulding
- pipes and conduits.

HDPE is mainly used for:

- blow moulding of:
  - household chemical bottles
  - industrial drums
  - liquid food bottles
  - drugs, cosmetics and toiletries
- injection moulding of:
  - crates and totes
  - food and beverage containers
  - housewares
  - industrial and shipping pails
- films for food packaging and retail bags
- sheets
- pipes and conduits
- rotomoulding.

Among other applications, let us quote, for example:

- films for agricultural, industrial or general-purpose uses
- fuel tanks for the automotive industry
- moulded basins, bottles, stoppers, toys, hollow parts, small electric equipment, pallets, street furniture, seats
- large-sized objects: cisterns, tanks, septic tanks, hulls of boats, canoes, buoys, sailboards, barrels, drums . . .
- gas, water or sewer pipes, sheaths
- crosslinked foams, extruded and moulded parts
- UHMWPE: gears, bearings, antifriction parts for light loads, prostheses

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