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Introduction to Polymeric Geomembranes

1.1 INTRODUCTION

The large number of commercially available geomembranes (or polymeric geosynthetic barriers) can make it challenging to select which geomembrane has the most appropriate combination of performance properties for a given application. Each type of geomembrane material has different characteristics that affect its installation procedures, durability, lifespan and overall performance. It is therefore necessary to match the project performance criteria with the right combination of properties of a particular geomembrane. Geomembrane materials are generally selected for their overall performance in key areas of chemical resistance, mechanical properties (elastic modulus, yield strength, puncture/tear resistance), weathering resistance, product life expectancy, installation factors and cost effectiveness.

The properties of polymeric geomembranes are determined mainly by their polymer structure (architecture of the chains), molecular weight (i.e. the length of the chains) and the crystallinity (packing density of the chains). Polymer crystallinity is one of the important properties of all polymers. Polymers exist both in crystalline and amorphous forms.

Common geomembranes can be classified into two broad categories depending on whether they are thermoplastics (i.e. can be remelted) or thermoset (i.e. crosslinked or cured and hence cannot be remelted without degradation) (see Table 1.1). Since thermoset geomembranes are crosslinked, they can exhibit excellent long-term durability.

When selecting a geomembrane for a particular application the following aspects need to be considered:

- choice of polymer;
- type of fabric reinforcement;
- colour of upper ply (e.g. white to maintain lower temperatures for sun exposed applications);
- thickness;

Table 1.1 Main plastic classifications for common geomembrane types

Thermoplastic geomembranes	Thermoset geomembranes	Combinations of thermoplastic and thermoset
HDPE, LLDPE	CSPE (crosslinks over time)	PE-EPDM
fPP	EPDM rubber	PVC-nitrile rubber
PVC	Nitrile rubber	EPDM/TPE (Trelleborg)
EIA	Butyl rubber	Polymer-modified bitumen
TPU, PVDF	Polychloroprene (Neoprene)	

- texture (e.g. smooth or textured for improved friction angles);
- product life expectancy;
- mechanical properties;
- chemical resistance;
- ease of installation.

Table 1.2 lists various advantages and disadvantages of common geomembrane types.

Firstly, geomembrane quality begins with base polymer resin selection. It is important to select or specify high-grade polymer resins that have been manufactured to meet the specific, unique demands encountered by geomembranes. Polymeric geomembrane properties are a function of the chemical structure of the base polymer resin, the molecular weight, the molecular weight distribution and the polymer morphology (e.g. the crystallinity). Next it is necessary to select the right combination of additives to protect the geomembrane, such as premium carbon black as well as antioxidant additives and stabilizers to ensure long life even in exposed conditions. Finally, it is necessary to select the most appropriate geomembrane manufacturing method.

1.2 VISCOELASTIC BEHAVIOUR

Polymers exhibit both viscous and elastic characteristics when undergoing deformation and hence are termed viscoelastic. Viscous materials (like honey), resist shear flow and strain linearly with time when a stress (e.g. in-service loading) is applied. Elastic materials strain (i.e. elongate) instantaneously when stretched and quickly return to their original state once the stress is removed (e.g. as in the case of EPDM liners). Viscoelastic materials have elements of both of these properties and, as such, exhibit time dependent strain.

Some phenomena in viscoelastic materials are:

1. If the strain is held constant, the stress decreases with time (this is called relaxation).
2. If the stress is held constant, the strain increases with time (this is called creep, as can be observed with HDPE liners).

Viscoelastic behavior comprised of elastic and viscous components is modelled as linear combinations of springs and dashpots, respectively.

The Maxwell model for viscoelastic behaviour can be represented by a viscous dashpot (a piston in oil) and an elastic spring connected in series, as shown in Figure 1.1(a). In

Table 1.2 Advantages and disadvantages of commonly used synthetic geomembranes

Geomembrane	Advantages	Disadvantages
HDPE	Broad chemical resistance Good weld strength Good low temperature properties Relatively inexpensive	Potential for stress cracking High degree of thermal expansion Poor puncture resistance
LLDPE	Better flexibility than HDPE Better layflat than HDPE Good multiaxial strain properties	Poor multiaxial strain properties Inferior UV resistance to HDPE Inferior chemical resistance to HDPE
fPP	Can be factory fabricated and folded so fewer field fabricated seams Excellent multiaxial properties Good conformability Broad seaming temperature window	Limited resistance to hydrocarbons and chlorinated water
PVC	Good workability and layflat behaviour Easy to seam Can be folded so fewer field fabricated seams	Poor resistance to UV and ozone unless specially formulated Poor resistance to weathering Poor performance at high and low temperatures
CSPE	Outstanding resistance to UV and ozone Good performance at low temperatures Good resistance to chemicals, acids and oils	Cannot be thermally welded after ageing
EPDM	Good resistance to UV and ozone High strength characteristics Good low temperature performance Excellent layflat behaviour	Low resistance to oils, hydrocarbons and solvents Poor seam quality
Butyl rubber	Good resistance to UV and weathering Good resistance to ozone	Relatively low mechanical properties Low tear strength Low resistance to hydrocarbons Difficult to seam
Nitrile rubber	Good resistance to oils and fuels (but not biodiesel)	Poor ozone resistance unless properly formulated Poor tear strength

this model if the polymer is put under a constant strain, the stresses gradually relax. That is, the tension in the spring (the stress) is gradually reduced by movement of the piston in the dashpot after a strong elongation (or displacement). Stress relaxation describes how polymers relieve stress under constant strain.

The Kelvin–Voigt model for viscoelastic behaviour also known as the Voigt model, consists of a viscous dashpot and Hookean elastic spring connected in parallel, as shown in Figure 1.1(b). It is used to explain the creep behaviors of polymers. When subjected

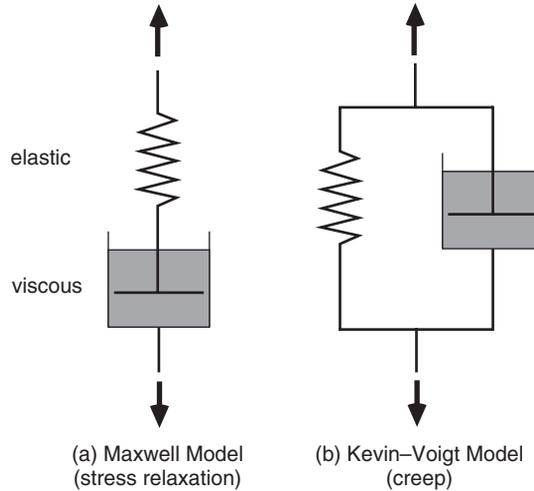


Figure 1.1 Polymers are viscoelastic materials having the properties of both viscous and elastic materials and can be modelled by combining elements that represent these characteristics. One viscoelastic model, called the Maxwell model, predicts behavior akin to a spring (elastic element) being in series with a dashpot (viscous element), while the Kelvin–Voigt model places these elements in parallel. Stress relaxation describes how polymers relieve stress under constant strain. Because they are viscoelastic, polymers behave in a nonlinear, non-Hookean fashion. This nonlinearity is described by both stress relaxation and a phenomenon known as creep, which describes how polymers strain under constant stress

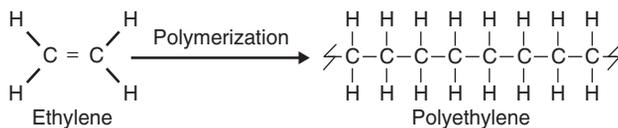
to a constant stress, viscoelastic materials experience a time-dependent increase in strain (i.e. change in length). This phenomenon is known as viscoelastic creep. In this model on the application of a force, the spring gradually expands until the spring force equals the applied stress. Creep describes how polymers strain under constant stress.

The temperature dependence of strain in polymers can also be predicted using this model. An increase in temperature correlates to a logarithmic decrease in the time required to impart equal strain under a constant stress. In other words, it takes less energy to stretch a viscoelastic material an equal distance at a higher temperature than it does at a lower temperature.

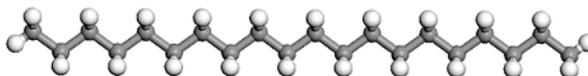
1.3 POLYMER STRUCTURE

Polymer structure describes the chemical makeup of the polymer chains. HDPE, for example, is comprised of linear molecules of repeating CH_2 groups as shown in Figure 1.2.

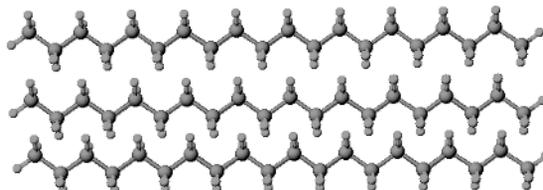
Chemical structures of the main classes of geomembranes are shown in Figure 1.3. Note that HDPE due to its regular, symmetrical structure is crystalline and quite stiff but by substituting one of the hydrogen atoms (shaded) with a bulky methyl group (as in flexible polypropylene) or an even more bulky chlorine atom (as in PVC) the crystallinity of the polymer is disrupted and the material becomes more flexible.



(a)



(b)



(c)

Figure 1.2 Schematic of (a) the chemical structure of ethylene gas and polyethylene, (b) the molecular structure of a single polyethylene chain or ‘backbone’ and (c) multiple HDPE chains showing the close packing behaviour of polyethylene chains which gives high-density polyethylene a semi-crystalline morphology and its high density.

The degree of incorporation of chlorine in the polymer structure also has a large bearing on the final properties. Chlorinated polyethylene (CPE) for instance contains between 36–42 wt% chlorine while PVC has 57 wt% chlorine. The low crystallinity of CPE allows high plasticizer and filler loadings and gives it rubbery elastomer properties. In the chlorination process the larger diameter chlorine atoms randomly replace the far smaller hydrogen atoms. The random substitution and the size discrepancy effectively disrupts the crystalline structure. Furthermore the incorporation of a polar plasticizer in both CPE and PVC destroys the dipole attraction between the chains and these polymers become very flexible and rubbery. The use of a ketone ethylene ester (KEE) polymeric plasticizer for PVC (in the case of EIA geomembranes) creates a material that is permanently plasticized since the plasticizer cannot be extracted or lost.

The incorporation of chemically active cure sites in the polymer structure such as diene in EPDM and the sulfonyl chloride group in the case of CSPE allows these materials to be crosslinked or cured to give thermoset elastomers. Where the partially (surface) fluorinated HDPE gives it increased chemical resistance, the polymerized polyvinylidene fluoride is a thermoplastic liner material that has outstanding chemical resistance to all those chemicals that can swell or oxidize HDPE (such as aromatic solvents and oxidizing acids).

1.4 MOLECULAR WEIGHT

Molecular weight (M_w) is basically the length of the polymer chains. Polymer chains are very long (made up of thousands of carbon atoms linked in series) and hence are

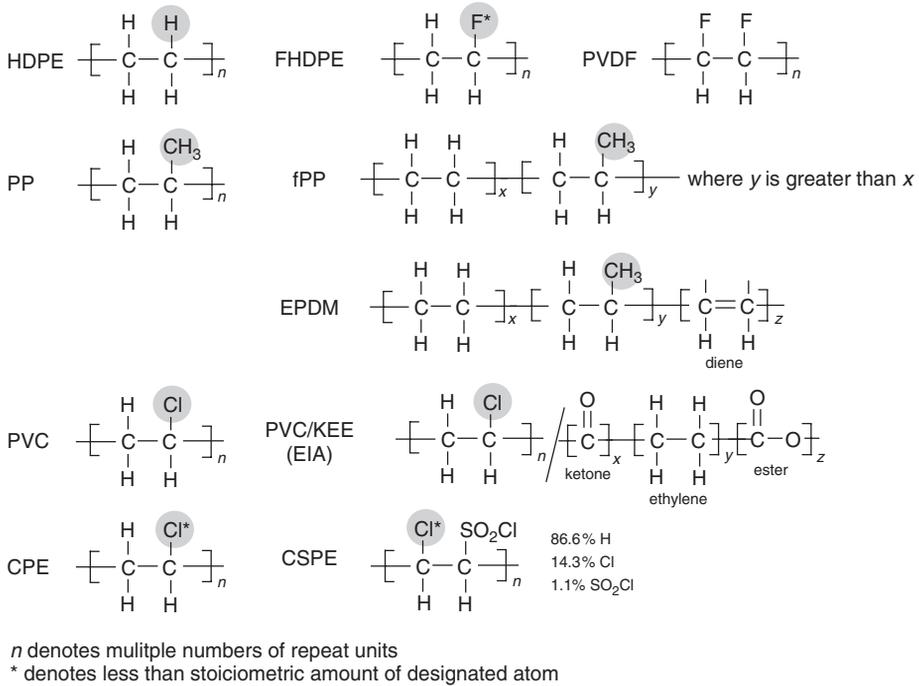


Figure 1.3 Chemical structures and repeat units of various geomembrane polymers. Note the most basic repeat unit is that of HDPE. Substitution of a hydrogen atom in the HDPE structure confers properties such as greater flexibility, greater polarity, greater solvent resistance and the ability to undergo crosslinking

also referred to as macromolecules. In general terms, as the polymer molecular weight increases, the geomembrane strength increases.

The molecular weight of the polymer can affect physical properties such as the tensile strength and modulus, impact strength, puncture resistance, flexibility and heat resistance as well as its long-term durability properties.

It is difficult to measure the molecular weight directly so generally a simpler way of expressing molecular weight is by the melt index (MI) (also referred to as melt flow index (MFI) or melt flow rate (MFR)). The melt index is inversely proportional to the polymer's molecular weight. For example, a low melt index value indicates higher molecular weight and stiffer melt flow behavior (i.e. higher melt viscosity) while a high melt index value indicates a lower molecular weight and easier melt flow (i.e. low melt viscosity) (Scheirs, 2000). Note: MFI is not applicable to PVC polymers.

Table 1.3 shows the effect of molecular weight and melt index on polymer properties.

HDPE geomembrane resins are generally high MW resins and therefore have low melt flow index values (see Figure 1.4). For this reason they are referred to as 'fractional melt' and 'HLMI' (high load melt index) resins. The term 'HLMI' HDPE refers to those polyethylene resins that should really be called High Molecular Weight resins with an HLMI of less than 15 g/10 min using ASTM D1238, Condition F (21.6 kg load).

Table 1.3 Effect of molecular weight and melt index on polymer properties

Property	As Molecular weight increases	As melt index increases
Molecular weight (chain length)	Increases	Decreases
Tensile strength (at yield)	Increases	Decreases
Tensile elongation	Increases	Decreases
Stiffness	Increases	Decreases
Impact strength	Increases	Decreases
Stress crack resistance	Increases	Decreases
Permeability	Decreases	Increases
Chemical resistance	Increases	Decreases
Abrasion resistance	Increases	Decreases
Processability	Decreases	Increases

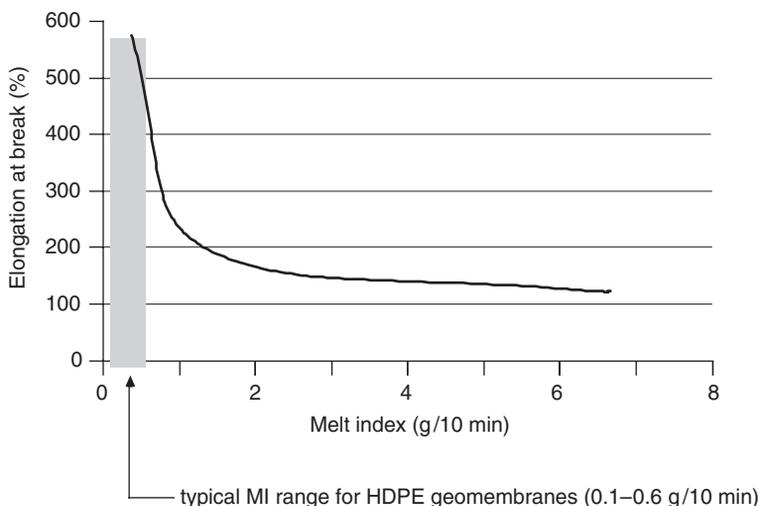


Figure 1.4 Relationship between melt flow index and % elongation at break for MDPE. Note the typical MI range for HDPE geomembranes (when tested with a 2.16 kg weight at 190 °C.)

The relationship between polymer molecular weight and melt index is summarized in Table 1.4

In addition to the length of the polymer chains (i.e. the molecular weight) the mechanical and physical properties of the plastics are also influenced by the bonds within and between chains, chain branching and the degree of crystallinity.

1.5 MOLECULAR WEIGHT DISTRIBUTION

The molecular weight distribution (MWD) is a fundamental polymer property which determines the processability and the end use properties of the polymer. Since an increase in the molecular weight of a polymer improves the physical properties, there is a strong

Table 1.4 Molecular weight and melt index relationship

Classification	Number of carbon atoms	Molecular (Mw) weight	MI (2.16 kg) standard melt index	MI (21.6 kg) high load melt index
Medium MW	7500–12 000	100 000–180 000	0.6–10	25–50
High MW	18 000–56 000	250 000–750 000	0.06–0.15	7–25

demand for polymers having high molecular weights. However, it is the high molecular weight molecules that render the polymer more difficult to process. A broadening in the molecular weight distribution tends to improve the flow of the polymer when it is being processed at high rates of shear as the low molecular weight tail acts as a “processing aid” for the higher MW chains.

Thus due to the high viscosity of higher molecular weight resins such as low HLMI HDPE used for geomembranes, the molecular weight distribution becomes a very important consideration in the processability of these HDPE resins. Resin manufacturers can tailor the molecular weight distribution (MWD) by catalyst and process selection. Geomembrane resins benefit from a broad to very broad distribution. While narrow distribution resins are tougher than broad distribution resins (at equivalent molecular weights), processability becomes easier as the MWD broadens. Table 1.5 shows the effect of molecular weight distribution on polymer geomembrane properties.

1.6 CRYSTALLINITY

In addition to the chemical structure, the properties of polymers are very dependent on the polymer morphology – particularly crystallinity.

The term crystallinity refers to the presence of crystalline regions where the polymer chains pack efficiently into dense regions that are impervious to both oxygen and chemicals (see Figures 1.5). Hence highly crystalline polyethylene has excellent chemical resistance and oxidative stability.

The ordered and aligned portions of the polymer chain form small regions that are called crystallites. The non-ordered regions are called amorphous. These amorphous regions that

Table 1.5 Effect of molecular weight distribution (MWD) on polymer geomembrane properties

Property	As molecular weight distribution broadens
Stiffness	Decreases
Impact strength	Decreases
Stress crack resistance	Increases
Melt strength	Increases
Processability	Increases

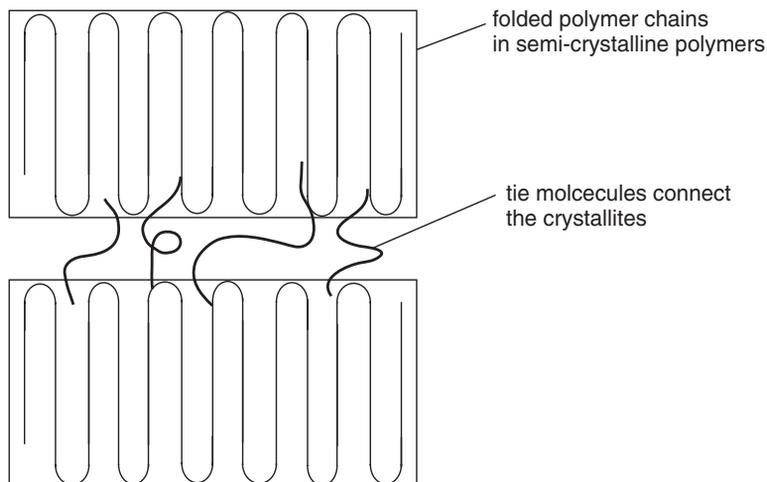


Figure 1.5 Schematic of crystallites in semi-crystalline polymers. The polymer chains fold tightly in densely packed crystallites which are impervious to oxygen and chemicals. The crystallites (or lamellae) are interconnected by tie molecules which span the amorphous regions

are not crystalline contain more random orientation of the polymer chains. The proportion of crystalline (ordered and tightly packed) regions to the amorphous (disordered) regions is expressed as the degree of crystallinity of the polymer.

! *Polymer chains can fold and pack together to form ordered (crystalline) regions. These regions where parts of the polymer molecules are arranged in regular order are called crystallites. In between these ordered regions molecules are arranged in a random disorganized state and these are called amorphous regions.*

! *Amorphous regions of a polymer are made up of randomly coiled and entangled chains. Amorphous polymers have lower softening points and are penetrated more by solvents than are their crystalline counterparts. PVC represents a typical amorphous polymer.*

The role of crystallinity is very important in explaining the behavior of polymeric geomembranes. The amount of crystallinity of geomembrane materials varies from nil in the case of PVC, to as high as 55–65% for HDPE (see Table 1.6).

The degree of crystallinity has a pronounced effect on the performance properties of the geomembrane, especially the mechanical properties and chemical resistance. The tightly packed molecules within the crystallites of HDPE, for example, creates dense regions with high intermolecular cohesion and these areas are resistant to penetration by chemical, gases and vapours. In contrast the complete lack of crystallinity of PVC geomembranes makes them susceptible to permeation and solvation by small solvent molecules.

Table 1.6 Typical % crystallinity values for various geomembrane polymers

Polymer	Crystallinity (%) (average values)
HDPE	55
MDPE	40
LLDPE	15
VLDPE	10
FPP	5
CPE	1–2
PVC	0

 *The highly crystalline nature of HDPE is responsible for its higher density and stiffness, as well as its low permeability and high chemical resistance.*

HDPE is semi-crystalline but introducing an alkene comonomer (e.g. butene or hexene) into the polymer backbone gives side chains that reduces the crystallinity. This in turn has a dramatic effect on polymer performance, which improves significantly as the side-chain branch length increases up to hexene, and becomes less significant with octene and longer chains. It is by manipulating this side branching that various grades of polyethylene varying in crystallinity are produced.

The greater number of crystalline regions is what differentiates HDPE from its lower density cousins such as LLDPE, MDPE, LDPE and VLPE. This semi-crystalline microstructure of HDPE imparts excellent chemical resistance and high strength; however it also makes HDPE susceptible to environmental stress cracking (ESC). fPP, CPE and PVC owing to their low crystallinities are more flexible and not susceptible to ESC (see Figure 1.6).

Polymer chains with side branches (e.g. LLDPE) or irregular pendant groups (e.g. PVC, CSPE) cannot pack together regularly enough to form crystallites. This is the reason why LLDPE and VLDPE, which have a controlled number of side branches, have much lower crystallinities than HDPE.

HDPE crystallizes from the melt under typical conditions as densely packed morphological structures known as spherulites. These are small spherical objects (usually from 1 to 10 μm) in diameter composed of even smaller structural subunits: rod-like fibrils that spread in all directions from the spherulite centres, occupying the spherulite volume. These fibrils, in turn, are made up of the smallest morphological structures distinguishable, small planar crystallites called lamellae. These crystallites contain folded polymer chains that are perpendicular to the lamella plane and tightly bend every 5 to 15 nm (see Figure 1.7).

Lamellae are interconnected by a few polymer chains, which pass from one lamella, through a small amorphous region, to another. These connecting chains, or tie molecules, are ultimately responsible for mechanical integrity and strength of all semi-crystalline polymer materials. Crystalline lamellae offer the spherulites rigidity and account for their high softening temperatures, whereas the amorphous regions between lamellae provide flexibility and high impact strength to HDPE products.

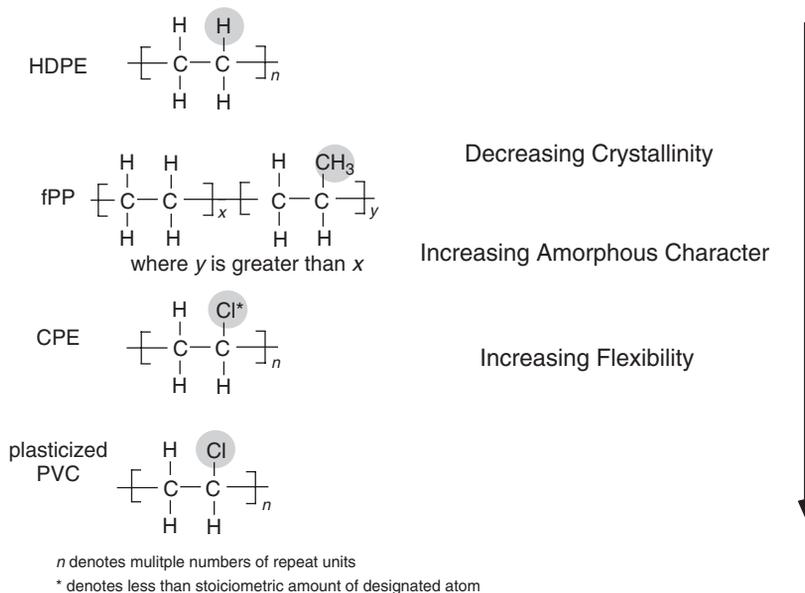


Figure 1.6 Effect that the substitution of a hydrogen atom in HDPE by substituents of increasing size (e.g. methyl group, chlorine atom) has on the crystallinity and the flexibility of the polymer

📌 Highly crystalline polymers are rigid, high melting and less affected by solvent penetration. Hence HDPE geomembranes which have some 55–60% crystallinity exhibit excellent solvent resistance. Crystallinity makes polymers strong, but also lowers their impact resistance. For instance, samples of HDPE prepared with crystallinities of 95% are extremely brittle.

An increase in the degree of crystallinity leads to a direct increase in rigidity and tensile strength at yield point, hardness and softening point and to a reduction in diffusion and permeability. However increasing crystallinity also means a reduction in the number of ‘tie’ molecules in the amorphous regions which are susceptible to chemical attack (e.g. oxidation) and tie chain pullout from the crystallites (i.e. stress cracking) (see Figure 1.8).

📌 Increasing crystallinity results in the following property attributes: increased tensile strength, increased stiffness or hardness, increased chemical resistance, decreased diffusive permeability (or vapour transmission), decreased elongation or strain at failure and decreased stress crack resistance.

In semi-crystalline polymers, the antioxidants reside in the amorphous regions which fortuitously are the same regions where oxygen can diffuse into cause oxidation. In contrast, the crystallites are too dense for either oxygen or antioxidant and diffuse into. The more amorphous polyolefins are more prone to oxidative degradation since oxygen can

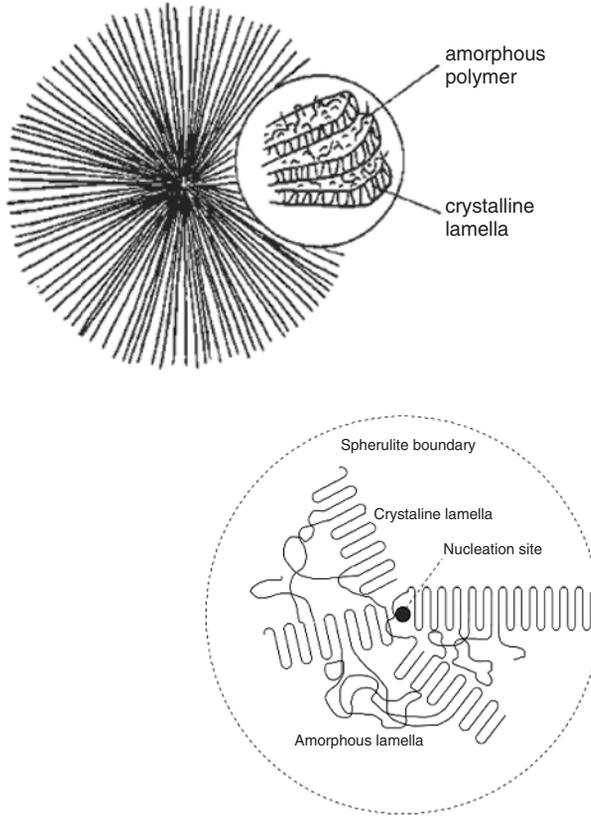
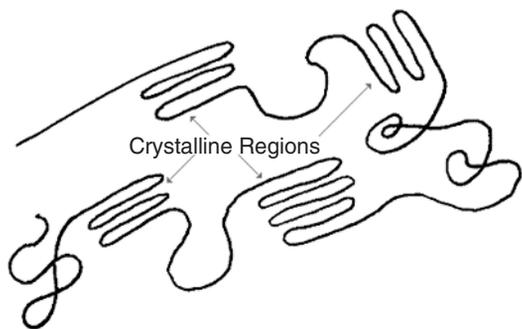


Figure 1.7 Schematic of spherulites in semi-crystalline polymers

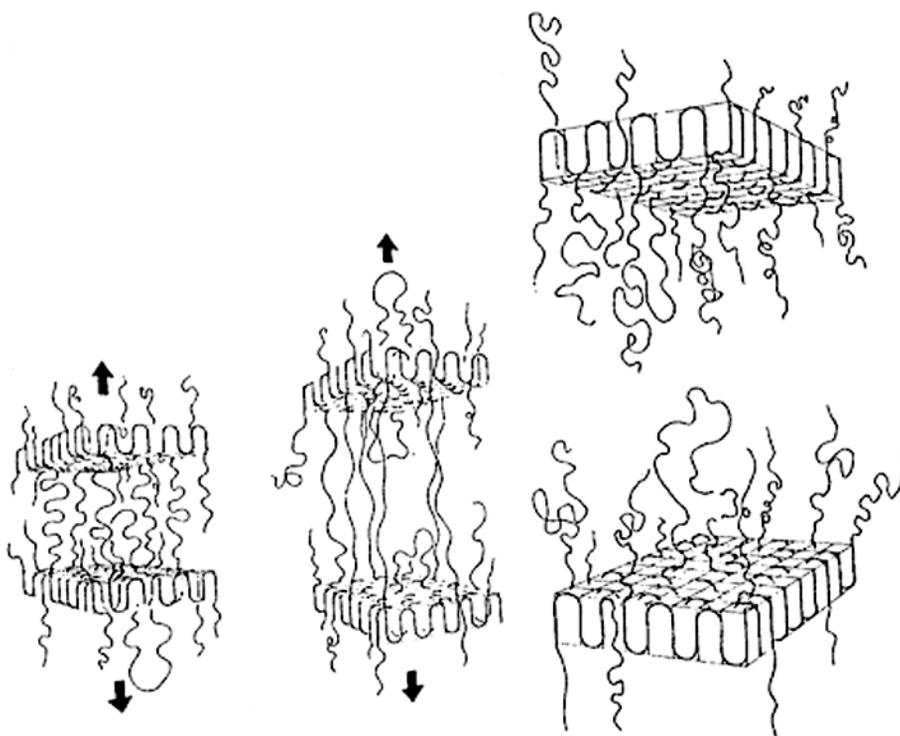
diffuse more freely throughout their entire structure and there is a greater volume of polymer that must be protected by the antioxidant. In addition, antioxidants can also diffuse more readily through and migrate more easily from amorphous polymers compared to their more crystalline forms (Scheirs, 2000).

📌 *Crystalline thermoplastics (also called semi-crystalline) include HDPE, LLDPE and polypropylene. In these materials the polymeric chains are folded in a crystal lattice. The folded chains form lamellae (plate-like crystals).*

📌 *Whilst the crystallites (i.e. tightly packed crystalline regions) are impervious to both oxygen and chemical ingress, the 'tie' molecules which interconnect the crystallites are susceptible to oxidation and chemical attack. The area in which the tie molecules reside is termed the amorphous region (i.e. disordered region) and these areas have lower density than the crystallites and so oxygen and opportunistic chemical can diffuse into these areas.*



(a)



(b)

Figure 1.8 Schematics of (a) the chain folding and packing behaviour of high-density polyethylene chains to form crystalline regions and (b) the crystalline regions or 'crystallites' in HDPE (which are interconnected by 'tie molecules') which can be pulled apart under the combined action of stress and a chemical agent (referred to as environmental stress cracking). Reprinted with permission from *Polymer*, Importance of tie molecules in preventing polyethylene fracture under long-term loading conditions by A. Lustiger and R. L. Markham, **24**(12), 1647. Copyright (1983) Elsevier

1.7 PROPERTIES OF POLYETHYLENES

Polyethylene is by far the most widely used polymer to manufacture geomembranes. Polyethylene resins are manufactured in very-low-density, low-density, linear low-density, medium-density and high-density varieties. The density range for all polyethylene geomembrane polymers falls within the general limits of 0.85 to 0.960 g/cm³.

Molecular weight, molecular weight distribution and crystallinity (i.e. density) are the three most important characteristics of polyethylene resins and play a major role in determining the durability and end-use performance properties of HDPE and LLDPE geomembranes.

Polyethylene is classified into several categories based on its density and branching. HDPE has little branching, giving it stronger intermolecular forces and higher tensile strength than lower density polyethylene, thereby making it ideal for geomembrane applications. HDPE is defined as having a density of equal to or greater than 0.941 g/cc.

The density of polyethylene is primarily controlled by the frequency and length of the side branches (which in turn are determined by the type and level of comonomer). The side branches prevent the PE chains from packing closely together, so the longer the side branches, the more open the structure and hence the lower the density. Homopolymer HDPE has a density greater than 0.960 g/cc while copolymers have densities less than 0.960 g/cc.



Note that true homopolymer HDPE is not used for geomembranes due to its tendency to undergo environmental stress cracking.

Typical comonomers are butene, hexene and octene which are carbon chains with 4, 6 and 8 carbons respectively. These comonomers are denoted as C4, C6 and C8 for simplicity. They all have a reactive double bond at the end of the chain and are referred to as alpha olefins. The 'olefin' indicates they contain a C=C bond in their structure while alpha indicates the double bond is between the first and second carbon atoms.

The type of comonomer used determines the end-use performance characteristics of the resin. Hexene and octene copolymers are tougher and more flexible; however butene copolymers are typically less expensive.

It is important to emphasize that HDPE geomembranes are actually manufactured using a polyethylene resin with a density 0.932–0.940 g/cm³ which falls into the MDPE category as defined in ASTM D-883. It is the addition of carbon black that pushes the final density of the geomembrane up into the density range between 0.941 and 0.950 g/cm³ which corresponds to a HDPE as defined in ASTM D-883. For this reason the 'HDPE' nomenclature is used to describe most black polyethylene geomembranes.



Note that 'HDPE' geomembrane resins are in fact MDPE base polymer with the addition of 2% carbon black, which raises its density into the classification range of HDPE.

The effect of increasing density on various PE geomembrane properties is shown in Table 1.7.

Table 1.8 lists the density classifications for polyethylene resins.

Table 1.7 Effect of density on PE geomembrane properties

Property	As density increases
Crystallinity	Increases
Tensile strength (at yield)	Increases
Stiffness	Increases
Impact strength	Decreases
Stress crack resistance	Decreases
Permeability	Decreases
Chemical resistance	Increases
Abrasion resistance	Increases
Processability	Decreases

Table 1.8 Density classifications for polyethylene resins

Polyethylene type	Defined density range (g/cc)
HDPE	0.941–0.965
MDPE	0.926–0.940
LLDPE	0.915–0.925
LDPE	0.910–0.915
VLDPE	0.880–0.910

HDPE is the most common field-fabricated geomembrane material primarily due to its low material cost, broad chemical resistance and excellent mechanical properties.

MDPE is a substantially linear polymer, with high levels of short-chain branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (e.g. 1-butene, 1-hexene and 1-octene).

LLDPE is a substantially linear polymer, with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (e.g. 1-butene, 1-hexene and 1-octene). As its name implies, Linear Low Density Polyethylene is a lower density polymer ($<0.939 \text{ g/cm}^3$), with increased material flexibility. LLDPE is mainly used for liners where large settlements are anticipated for long term consolidation, such as for landfill covers. Capping contaminants with LLDPE geomembranes, not only makes it possible to control the release of carbon dioxide and methane (by-products of the decomposition of organic matter), but allows their capture and reuse. The flexibility of the LLDPE is also useful for geomembrane liners that are installed on subgrades prone to differential settlement.

LLDPE has a higher tensile strength and higher impact and puncture resistance than LDPE. It is very flexible and elongates under stress. It can be used to make thinner sheets, with better environmental stress cracking resistance. It has good resistance to chemicals and to ultraviolet radiation (if properly stabilized). However it is not as easy to process as LDPE, has lower gloss and a narrower operating range for heat sealing. Hence it finds application in plastic sheets (where it permits use of lower thickness profile than comparable LDPE), coverings of cables, geomembranes and flexible tubing.

LLDPE geomembranes are available in a smooth, textured or single textured finish. The comonomers used to produce the resin can include hexene or octene.

Low-density polyethylene (LDPE) has very poor environmental stress crack resistance and rather poor mechanical properties and so it does not find application as a geomembrane. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack to form a dense crystal structure as well. It has therefore less strong intermolecular forces, as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility.

VLDPE is most commonly produced using metallocene catalysts and is a highly flexible and ductile material.

1.8 STRESS–STRAIN BEHAVIOUR OF POLYMERS

The stress–strain behaviour of polymers used to manufacture geomembranes is largely determined by the properties discussed above, namely the molecular weight, molecular weight distribution and crystallinity or density.

Figure 1.9 shows a typical stress–strain curve for HDPE which identifies the following:

- the linear elastic region (where it obeys Hooke’s Law);
- the plastic region where the polymer draws and extends;
- the yield stress;
- the ultimate strength (or tensile strength at break);
- the modulus of elasticity (i.e. the gradient of the initial linear slope).

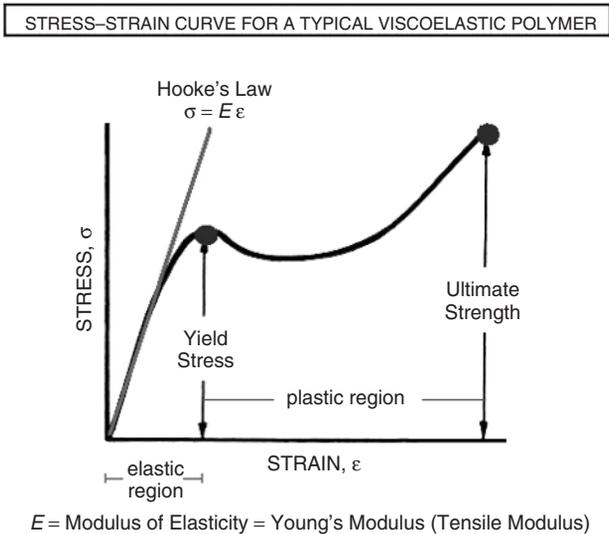


Figure 1.9 Stress–strain curve showing elastic and plastic regions

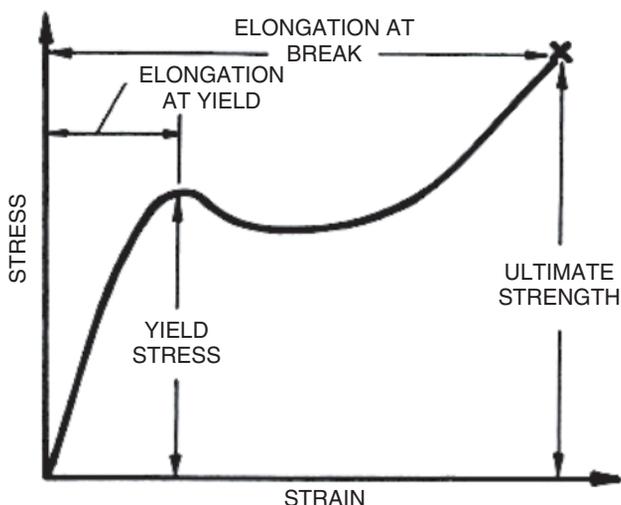


Figure 1.10 Stress–strain curve for HDPE showing main tensile test value parameters

Figure 1.10 is a similar stress–strain curve which also identifies the elongation at yield (also known as the yield strain) and the elongation at break (also known as the breaking strain).

Figure 1.11 shows the stress–strain curves for various polymer types. If the load rises linearly to fracture with no plastic deformation then the material is said to be brittle as is the case for PVC liners where the plasticizers have been extracted or, for HDPE geomembranes after extensive oxidation. More commonly though the behaviour of geomembranes is ductile but may exhibit brittle behaviour depending on the temperature. The brittle transition occurs at sub-zero temperatures for common geomembranes (see section on low temperature properties) (Scheirs, 2000). For geomembranes applications either hard and tough (e.g. HDPE) or soft and tough (e.g. CSPE, fPP, EIA) polymers are the most suitable.

1.8.1 YIELD BEHAVIOUR

‘Yield’ is defined as the onset of plastic deformation in a polymer under an applied load. This is an important parameter because it represents the practical limit of use more than does ultimate break or rupture. The yield properties depend on the polymer crystallinity and the polymer morphology. The yield behaviour also depends on the test conditions used. The yield properties vary with both the test temperature and the speed of the test. For this reason it is very important that tensile testing of polymer geomembranes be conducted at 23 °C where possible. This may therefore cast doubt on field tensiometer measurements where higher or lower temperatures might be encountered. Since the speed of the tensile test is also critical, the tensile test speed (also known as the *crosshead speed* and determined by the strain rate) must be standardized and defined (Scheirs, 2000).

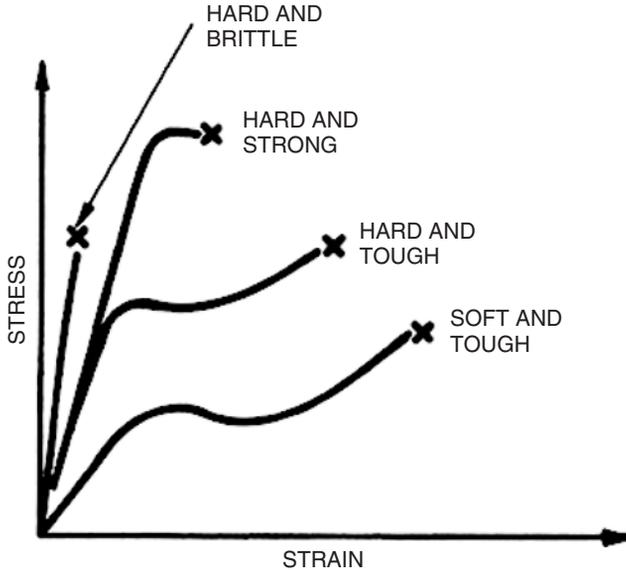


Figure 1.11 Stress–strain curves for various polymer types

1.8.2 PLASTIC DEFORMATION

‘Plastic deformation’ is the deformation that remains after a load is removed from a polymer sample. It is also called permanent deformation or non-recoverable deformation. Under small enough loads less than the yield stress the deformation is elastic and is recovered after the load is removed (i.e. the specimen returns to its original length). Yielding thus represents the transition from elastic to plastic behaviour. Consider a HDPE geomembrane sample under an applied tensile load. The length of the specimen will increase (as measured by the elongation). As the elongation increases, the load at first increases linearly but then increases more slowly and eventually passes through a maximum where the elongation increases without any increase in load (as in Figure 1.10). This peak in the stress–strain curve (i.e. the load–elongation curve) is the point at which plastic flow (permanent deformation) becomes dominant and is defined as the yield point. Not all polymers exhibit a defined yield point such as that exhibited by HDPE. PVC, for example, shows no obvious yield point in the stress–strain curve.

1.8.3 STRESS

The shape and magnitude of the load–elongation curve depends on the particular polymeric geomembrane being tested. Rather than load, the properly normalized variable is stress which is defined as the load per unit cross-sectional area of the test specimen. Stress therefore has units of pressure (1 MPa = 1 MN/m² = 145 psi).

1.8.4 STRAIN

Rather than quoting elongation, the proper normalized variable is strain which is the extension divided by the initial length. Strain is therefore dimensionless whereas elongation is expressed as a percentage.

1.8.5 TYPES OF LOADING

The most common type of loading used for testing polymeric geomembranes is *uniaxial tension* but other types of loading are arguably more important such as compression, hydrostatic compression and uniaxial (i.e. multiaxial tensile) loading. The simplest variation of the tensile test is the uniaxial compression test which should not be confused with hydrostatic compression in which the load is applied from all sides. It has been found that compressive stresses are higher than tensile stresses for a given strain value.

1.8.6 TEMPERATURE EFFECTS

The shape and magnitude of the stress–strain curve is very dependent on temperature. As the temperature increases, the yield stress, elastic modulus (i.e. stiffness) and yield energy all decrease while the yield strain (elongation at yield) increases (see Figure 1.12).

1.8.7 STRAIN RATE EFFECTS

Strain rate determines to the speed of the application of force on the material being tested. High strain rates (i.e. high testing speed) have the effect of making the polymer behave in a more brittle fashion – in the same way that reducing the temperature makes the polymer stiffer and more brittle (Figure 1.13).

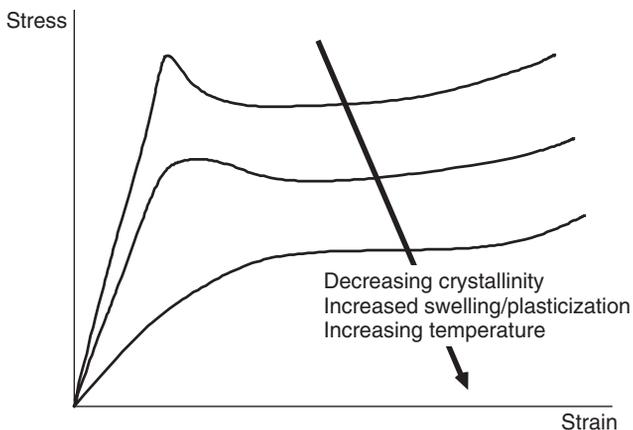


Figure 1.12 Effect of swelling and increased temperature on the stress strain properties of HDPE geomembranes. The material becomes softer and more rubbery but loses its tensile strength

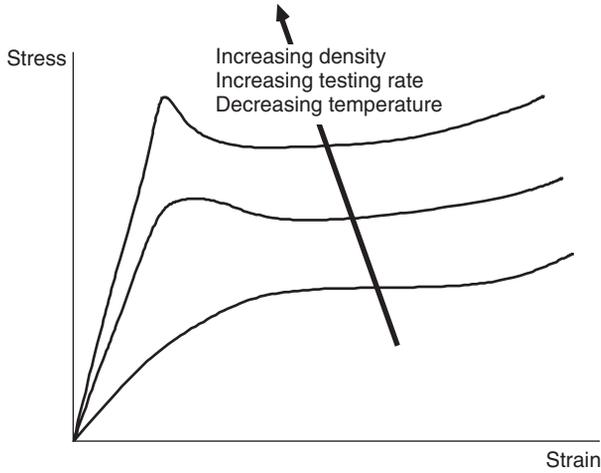


Figure 1.13 Effect of increasing density or increasing testing rate (i.e. strain rate) or decreasing temperature on the stress–strain properties of HDPE geomembranes. The material becomes stiffer and stronger as the density or testing speed increase or as temperature is decreased

Table 1.9 Melting points of various polymer resins

Polymer	Melting point (°C)
Poly(ethylene vinyl acetate) (EVA)	85
Metallocene polyethylene (mPE)	90–100
Low-density polyethylene (LDPE)	108
Linear low-density polyethylene (LLDPE)	125
High-density polyethylene (HDPE)	130
Flexible polypropylene (fPP)	150

1.9 MELTING POINTS

Polymer geomembrane resins have very different melting points as shown in Table 1.9. The polymer melting point (or more correctly the melting range) is of importance during thermal welding; particularly when welding different geomembrane materials to each other.

REFERENCES

Scheirs, J., *Compositional and Failure Analysis of Polymers: A Practical Approach*, John Wiley & Sons, Ltd, Chichester, UK, 2000, 766 pp.