3

Gel-spun high-performance polyethylene fibres

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3.1 Introduction

Gel-spun polyethylene fibres are ultra-strong, high-modulus fibres that are based on the simple and flexible polyethylene molecule. They are called high-performance polyethylene (HPPE) fibres, high-modulus polyethylene (HMPE) fibres or sometimes extended chain polyethylene (ECPE) fibres. The gel-spinning process uses physical processes to make available the high potential mechanical properties of the molecule. This has been quite successful but there is still ample room for improvement.

Owing to low density and good mechanical properties, the performance on a weight basis is extremely high. The chemical nature of polyethylene remains in the gel-spun fibre and this can both be positive and a limitation: abrasion, flexlife, etc. are very high but the melting point is sometimes too low for certain applications.

3.2 Manufacture

3.2.1 Molecular character

Gel-spun high-performance polyethylene fibres are produced from polyethylene with a very high molecular weight (UHMW-PE). This material is chemically identical to normal high-density polyethylene (HDPE), but the molecular weight is higher than the commonly used PE grades. It is in the range that is used in abrasion-resistant engineering plastics.

Different from all other high-performance fibres, the molecules in high-performance polyethylene fibres are not 'preformed' to form high tenacity and modulus fibres. In aramids and comparable fibres, the molecules tend to form rod-like structures and these need only be oriented in one direction to form a strong fibre. Polyethylene has much longer and flexible molecules and only by physical treatments can the molecules be forced to assume the straight (extended) conformation and orientation in the direction of the fibre.

All the physical and chemical properties of polyethylene remain in the fibres. The differences result from the high chain extension (stretching), the high orientation and the high crystallinity.

The gel-spun fibres have properties that are superior to those made by solid-state processes.

3.2.2 Gel-spinning

High performance polyethylene fibres are commercially produced under the trade names *Dyneema* by DSM High Performance Fibers in the Netherlands and by the Toyobo/DSM joint venture in Japan, and *Spectra* by Honeywell (formerly Allied Signal or Allied Fibers) in the USA. The basic theory about what a super-strong polyethylene fibre should look like was already available in the 1930s from the ideas of Carothers, but it took almost half a century to produce HPPE fibres.[1]

The basic theory of how to produce a super-strong fibre from a polymer such as polyethylene is easy to understand. In normal polyethylene the molecules are not orientated and are easily torn apart. To make strong fibres, the molecular chains must be stretched, oriented and crystallised in the direction of the fibre. Furthermore, the molecular chains must be long to have sufficient interaction and for this reason polyethylene with an ultra-high molecular weight (UHMW-PE) is used as the starting material. Usually extension and orientation are realised by drawing. The problem is that spinning these fibres from the melt is almost impossible due to the extremely high melt viscosity. Furthermore, the drawing of a melt-processed UHMW-PE is only possible to a very limited extent owing to the very high degree of entanglement of the molecular chains. In the gel-spinning process these two problems are solved: the molecules are dissolved in a solvent and spun through a spinneret. In the solution the molecules become disentangled and remain in that state after the solution is spun and cooled to give filaments. Because of its low degree of entanglement, the gel-spun material can be drawn to a very high extent (superdrawn). As the fibre is superdrawn, a very high level of macromolecular orientation is attained (see Fig. 3.1) resulting in a fibre with a very high tenacity and modulus. In the processes used by DSM and Honeywell, high-molecular weight polyethylene is spun using relatively low concentrations. In the 1980s, Mitsui Petrochemical used the gel-spinning process to produce a relatively strong fibre based on a lower molecular weight PE and a higher concentration. This process is now not in commercial use.

In 1979 DSM invented and patented the fibre and the gel-spinning process to produce it (Smith and Lemstra.)[2] Several further patents

3.1 Macromolecular orientation of HPPE and normal PE.

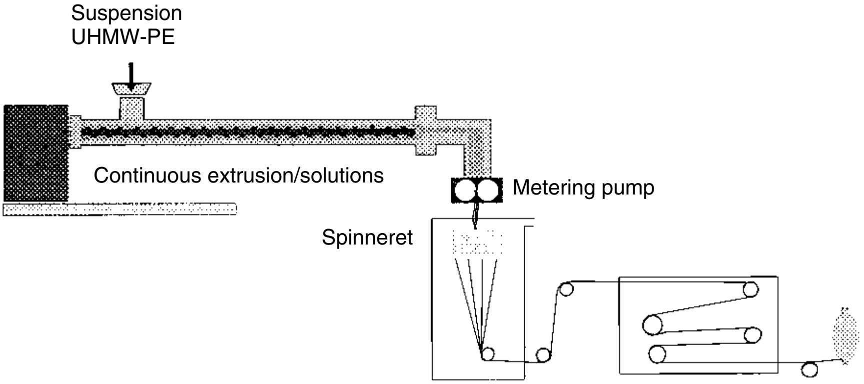
concerning this process have been filed in later years. *Dyneema* fibres have been in commercial production since 1990 at a plant at Heerlen, The Netherlands. The production of *Dyneema* fibres demands relatively little energy and uses no aggressive chemicals. The product can easily be recycled so environmental pollution from product and process is minimal.

DSM has a joint venture agreement with Toyobo Co. for commercial production in Japan. In the USA, DSM has granted a license to Allied Signal, now Honeywell. The latter produces the *Spectra* fibre at Petersburg (Va).

Since the start of commercial production, the performance of the *Dyneema* and *Spectra* fibres has been improved considerably. New grades have been introduced and a significant potential for further improvements is still present. Gel-spinning of HPPE fibres is a process that hinges on mechanical and physical parameters, not on chemistry. This makes it relatively easy to produce a wide range of fibre grades. The gel-spun fibres are characterized by a high degree of chain extension, parallel orientation greater than 95% and a high level of crystallinity (up to 85%). This gives the fibres their unique properties.

3.2.2.1 Gel-spinning process

Figure 3.2 shows a diagram of the gel-spinning process.[3]



3.2 Gel-spinning process.

The main steps in the process are:

- The continuous extrusion of a solution of ultra high-molecular weight polyethylene (UHMW-PE).
- Spinning of the solution, gelation and crystallization of the UHMW-PE. This can be done either by cooling and extraction or by evaporation of the solvent.
- Superdrawing and removal of the remaining solvent gives the fibre its final properties but the other steps are essential in the production of a fibre with good characteristics.

In the gel-spinning process, not only do all the starting parameters have an influence on the final properties of the fibre, the different process steps also influence all the following stages in the production of the fibre. So, starting from the same principles, *Dyneema* and *Spectra* may use very different equipment to produce comparable fibres.[4]

3.2.2.2 Feedstock polymer

Polyethylene is a flexible polymer with a very weak interaction between the molecular chains as only the Van der Waals forces are active. This interaction is so weak that for strong fibres, ultra-long chains with a high overlap lengths are required. The starting material for the high-performance polyethylene fibres is polyethylene with an average molecular weight of one million or more. The higher the molecular weight, the higher the strength that can be obtained. Improvements in equipment and processing parameters have made it possible to increase the molecular weight over the years.

Both the average molecular weight and the molecular weight distribution are critical parameters. Chains that are too long hinder the drawing step; short chains are less effective in the transmission of the load in the final fibre. Branches on the chains also interfere with the drawing; however, it has been shown that a limited number of branches gives a better performance.

3.2.2.3 Spinning solution

With long-chain, flexible polymers the high orientation required can be obtained by drawing up to a very high draw ratio (50–100 times). Melt-processed UHMW-PE can be drawn up to five times only, as the interaction between the molecular chains is too high because of the molecular entanglements. In solution, the molecules disentangle but there remain a number of cross-overs determined by the concentration and the length of the molecules. The flexible molecules assume a roughly spherical shape with a diameter proportional to the cubic root of the molecular weight. For the UHMW-PE chains the diameter of such a ball is about 1% of the total chain length.

As soon as strain is applied when the solution is pressed through the spinneret, the molecules are forced into more elongated form. This is the first step in the orientation process and the geometry of the spinneret has been thoroughly studied in DSM's research into improvements to the properties of the *Dyneema* fibre.

For maximum fibre strength, the polyethylene molecules should be as long as possible. From an economic point of view the concentration of the solution should be as high as possible. However, these two factors together result in a solution that has a viscosity that is far too high to spin. Careful optimisation of these parameters is an essential part of the process.

3.2.2.4 Gelation and crystallization

The solvent used in the polyethylene gel-spinning process should be a good solvent at high temperatures (>100 °C) but at lower temperatures (<80 °C) the polymer should easily crystallize from the solution. After the spinneret, the solution is cooled in the quench, the solvent is removed and a gel fibre is formed. This can be done by evaporation or by extraction of the solvent.

From a diluted solution, polyethylene crystallizes in the form of flat crystals of about 20 nm thickness, in which the chains are neatly folded. In these crystals the C-axis or chain axis is perpendicular to the crystal (lamella) surface. The crystal structure is orthorhombic, which implies that the crystal axes are at right angles, two by two. The theoretically attainable modulus and tenacity of fibres can be derived from that of these polyethylene crystals.

The spatial structure of the polyethylene molecules at the moment of crystallization is critical for obtaining good drawability. This spatial structure is determined by the number of entanglements in the solution, the shape of the spinneret and, of course, the conditions in the quench. Together these parameters determine the necessary overlap of several different molecular chains in a single lamella. Control of the molecular overlap is a critical factor determining the drawability.

Between a single crystal and a fibre there is quite a long way to go. Lamellar crystals with folded chains do not form suitable building blocks for a strong fibre. Long, thread-like crystals (fibrils) with extended chains are much better suited for this purpose. After the removal of the solvent, the fibres consist of microcrystalline crystals embedded in non-crystalline material. In the subsequent drawing stage, the apparently random crystals and most of the non-crystalline material is transformed into a highly crystalline, highly oriented fibre.

3.2.2.5 Drawing

The final properties of the fibre in the gel-spinning process are achieved in the superdrawing stage. All the preceding steps are needed to make this possible. The strength and modulus are directly related to the draw ratio. The maximum attainable draw ratio appears to be related to the molecular weight and the concentration. The attainable draw ratio increases with decreasing concentration, but for each molecular weight there is a minimum concentration below which drawing is not possible, due to insufficient molecular overlap.

The explanation for this drawing behaviour is generally sought in the number of chain–chain entanglements. In a melt or in a concentrated solution of polyethylene with a very high molecular weight, there is a high concentration of entanglements. This makes it impossible to achieve a high draw ratio with the corresponding properties. On the other hand, if no entanglements are present due to too low a concentration, the gel fibre will break. The elasticity is then too low and the forces in the spinning process cannot be passed on over a great length. The fibre will break before it is drawn. A very low concentration is, of course, not interesting in a commercial process, but a trade-off has to be made between two conflicting parameters: a high molecular weight to reach a higher tenacity and a high concentration in order to keep the process feasible.

Gel-spinning a high performance polyethylene fibre has proven to be a highly interrelated process. At each step, not only the starting parameters and local conditions determine the result, but also all the preceding process steps are an important part of the polymer's history. Polyethylene as a polymer has a very long relaxation time – a long memory.

3.2.3 Other gel-spun fibres

The gel spinning process can also be used for other polymers. To obtain a strong fibre it is necessary that the gel fibre can be drawn to get a high orientation of the molecules, so only a limited number of polymers are suitable. Most polymers have too many side chains or possess chains with a strong interaction and so resist drawing below the melting temperature. Polymers such as PECO (a copolymer from ethylene and carbon monoxide) and PAN (polyacrylonitrile) have been tested, but only gel spun PVA (polyvinyl alcohol) is commercially available. Kuraray from Japan uses a gel-spinning process to produce a PVA fibre. The main characteristics of this fibre, however, are not its high mechanical properties, but its easy solubility in water.

3.3 Fibre characteristics

3.3.1 Fibre form

Dyneema and *Spectra* are produced as a multifilament yarn. The titre of the monofilaments varies from about 0.3 denier per filament (dpf) (0.44 dtex) to almost 10 dpf (11 dtex). Tenacity of one filament may well be over 5 N/tex, and the modulus can be over 120 N/tex.

Staple fibre is not produced as such. Stretch broken and cut fibres are used by specialised companies.

Most fibre grades have a more or less circular cross-section. The fibre skin is smooth.

3.3.2 Structure and morphology

The fibre is highly crystalline; the crystallinity is typically >80%. The crystal domains, mainly orthorhombic with a small contribution of monoclinic, are highly extended in the fibre direction. The crystal domains are organised in nano- or microfibrils, which in their turn form macrofibrils. The larger part of the non-crystalline fraction is in the form of an interphase that is characterised by a high density, a high orientation and restricted mobility of the molecular chains.

3.3.3 Commercially available fibres

The product portfolio for *Dyneema* and *Spectra* at the end of 2000 is shown in Table 3.1. The reported physical properties are representative of published information from the fibre manufacturers. These values are influenced by testing methods and hence the direct comparison of properties is not always correct.

Table 3.1 Commercially available HPPE filament yarns

	Density (kg/m^3)	den/fil (dpf)*	Tenacity (N/tex)	Modulus (N/tex)	Elongation to break (%)
DSM HPF					
Dyneema SK60	970	1	2.8	91	3.5
Dyneema SK65	970	1	3.1	97	3.6
Dyneema SK75	970	2	3.5	110	3.8
Dyneema SK76	970	2	3.7	120	3.8
Toyobo					
Dyneema SK60	970	1	2.8	91	3.5
Dyneema SK71	970	1	3.5	122	3.7
Honeywell					
Spectra 900	970	10	2.6	75	3.6
Spectra 1000	970	5	3.2	110	3.3
Spectra 2000	970	3.5	3.4	120	2.9

* dtex values are 10% larger than dpf.

3.4 Properties

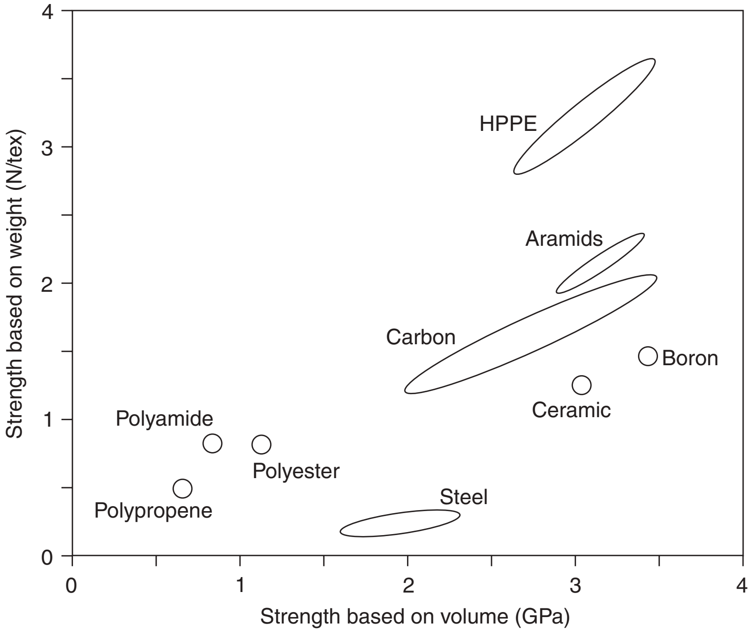
3.4.1 Density

HPPE fibres have a density of 970 to 980 kg/m^3, typical for highly crystalline linear polyethylene.

3.4.2 Tensile properties

The primary properties of the *Dyneema* and *Spectra* fibres are high strength and high modulus in combination with the low density. HPPE fibres have a density slightly less than one, so the fibre floats on water. Whereas the strength and modulus are already very high in engineering units (GPa), the combination with the low density makes the specific strength or tenacity and specific modulus extremely high. The tenacity is 10 to 15 times that of good quality steel and the modulus is second only to that of special carbon fibre grades and high modulus PBO. Elongation at break is relatively low, as for other high-performance fibres, but owing to the high tenacity, the energy to break is high.

Figure 3.3 gives fibre strength in textile units (N/tex) and in engineering units (GPa). Textile units relate the strength to the weight of the fibre whilst engineering units refer to the cross-section and the volume of a fibre. It is clear from this diagram that the combination of low density and high strength makes *Dyneema* and *Spectra* unique products. The diagram also



3.3 **Strength based on weight *vs* strength based on volume of various fibres.**

shows that HPPE fibres are not only first choice in weight saving, but that their use can also give volume saving.

In Table 3.2, the theoretical maximum values for tenacity and modulus are shown for a number of polymer fibres (Yasuda *et al.*).[5] It is clear that for HPPE substantial improvements in properties are still possible.

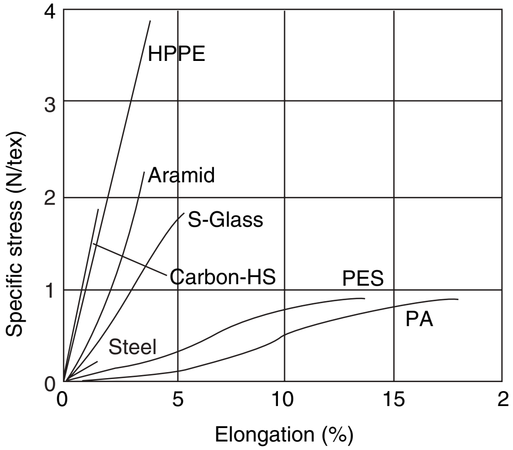
In Fig. 3.4 the specific stress and the elongation of various fibres are shown. The areas below the curves are the energy-absorbing capacities of the fibres.

The strength of a fibre can also be expressed as the free breaking length. The free breaking length is the theoretical length of a fibre, yarn or rope at which it breaks under its own weight when hanging freely. This free breaking length is material related and corresponds to the tenacity. Free breaking length is independent of the thickness of the fibre or the rope. Figure 3.5 is an artist's impression of the free breaking length of different fibres. *Dyneema* and *Spectra* would in theory reach to a satellite's orbit.

Figure 3.6 shows the specific strength versus the specific modulus and illustrates why HPPE fibres give veritable high performance. The high specific modulus is also relevant in ballistic protection. The sonic velocity in the fibre determines the speed of spreading energy on ballistic impact and the sonic velocity is calculated as the square root of the specific modulus.

Table 3.2 Theoretical and achieved properties of fibres

Polymer	Strength, theoretical		Strength, commercial		Modulus, theoretical		Modulus, commercial	
	GPa	N/tex	GPa	N/tex	GPa	N/tex	GPa	N/tex
PE	32	33	3.6	3.7	240	247	116	120
Aramid	30	21	3.3	2.3	183	127	120	83
PA-6	32	23	0.9	0.8	142	125	6	5
PES	28	20	1.1	0.8	125	90	14	10
PP	18	20	0.6	0.6	34	38	6	6



3.4 Fibre stress–strain curves. PES = polyester, PA = polyamides, HS = high strength.

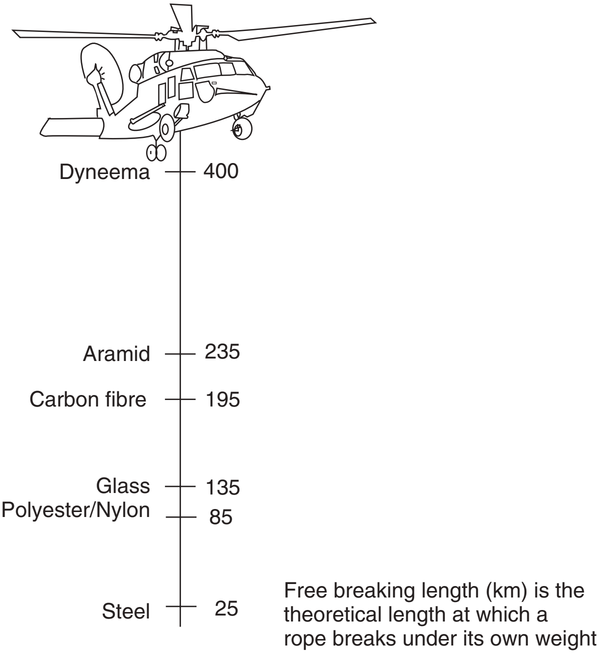
In contrast to the high tensile strength, the gel-spun fibre has a low compressive yield strength, approximately 0.1 N/tex.

3.4.3 Mechanical properties in the transverse direction

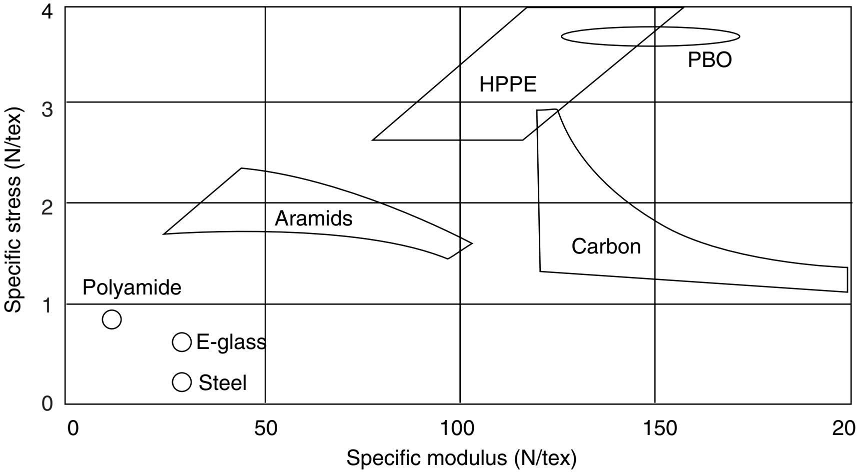
As all the chains in the fibre are aligned in the fibre direction, the mechanical properties are highly anisotropic. In the transverse direction the modulus and strength are much lower than that in the fibre direction. Table 3.3 gives estimated values.

3.4.4 Viscoelasticity

Polyethylene is a viscoelastic material, that is, the properties depend significantly on such variables as temperature and loading history.



3.5 Free breaking length of various fibres.



3.6 Specific strength *vs* specific modulus for various fibres.

Table 3.3 Transverse properties of HPPE fibres

Transverse elastic modulus	3 GPa
Transverse compressive yield stress	0.05 GPa
Transverse tensile strength	0.03 GPa

One feature is that the mechanical properties of HPPE fibres such as tensile strength (or tenacity), tensile modulus and elongation at break depend on the temperature and the strain rate. At high strain rates, or alternatively at low temperatures, both modulus and strength are significantly higher than the values given in the tables before. This is important in ballistic protection.

Another feature is that the fibre is prone to creep; the deformation increases with loading time, resulting both in a lower modulus and a higher strain at rupture. Creep is important, for instance, when ropes are under relatively high loads over a long period of time.

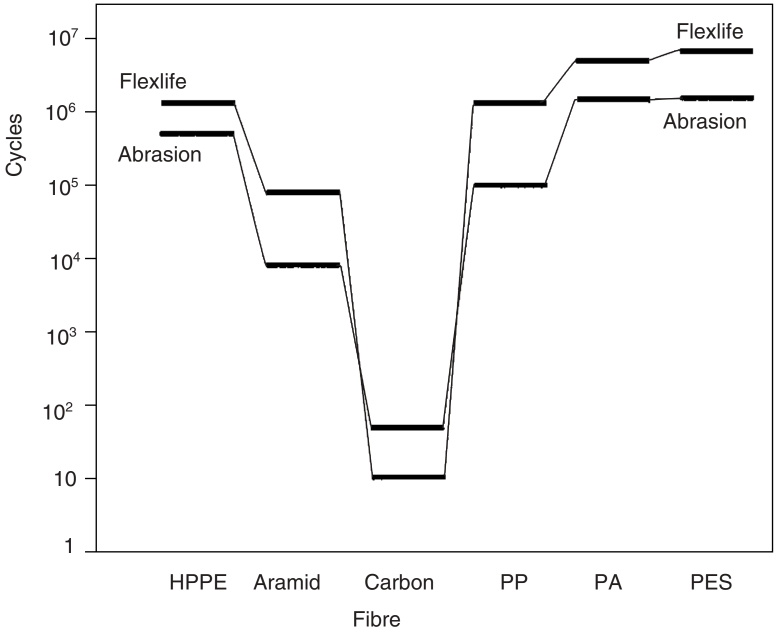
Creep values are not the same in all HPPE fibres but depend on choices made in the production process. Creep is not an important and controlled property in all the HPPE fibre types so it should not necessarily be constant in value in, for example ballistic fibre grades. For the *Dyneema* fibre grades that are used in ropes and comparable applications, there is a computer model that predicts creep in rope constructions (Smeets *et al.*[12]).

3.4.5 Energy absorption

Dyneema and *Spectra* fibres can absorb extremely high amounts of energy. This property is utilized in products for ballistic protection. But it makes the fibre equally suited for products such as cut-resistant gloves and motor helmets. The fibres can also be used to improve the impact strength of carbon or glass fibre-based composites. In these applications, not only the high tenacity is used but also the high energy absorption.

3.4.6 Fatigue

Fatigue is very important in, for example, rope applications. HPPE fibres are the first high-performance fibres that not only have a high tenacity but that also have tension and bending fatigue properties comparable with the commonly used polyamide and polyester grades in ropes. Carbon fibres and glass fibres have a high modulus and a brittle breaking mode, but HPPE fibres demonstrate that this is not an obvious combination. *Dyneema* and *Spectra* fibres have a high modulus but still are flexible and have a long flex



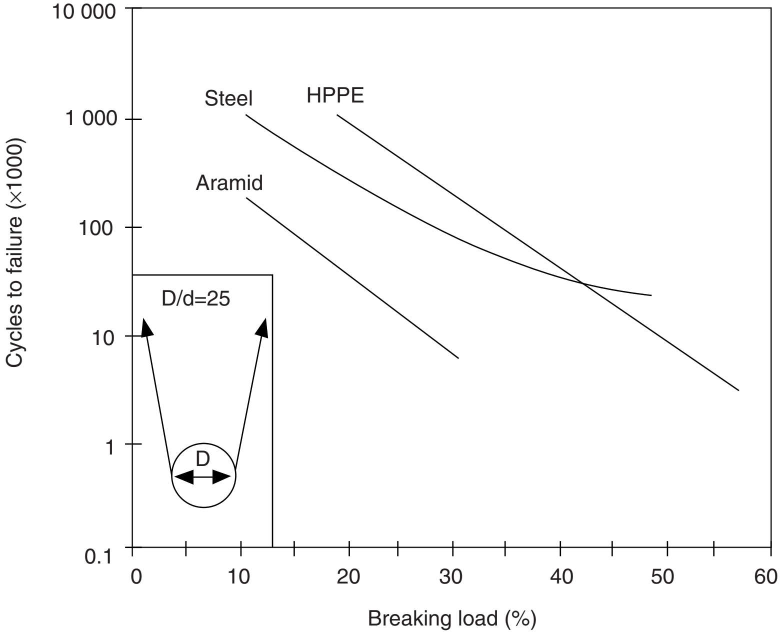
3.7 Abrasion and flex life of various fibres.

life (see Fig. 3.7). The good flexural fatigue resistance is related to the low compressive yield stress.

In tension fatigue testing, a rope is repeatedly loaded in tension. A typical example is loading to, for example 50% of its breaking load followed by relaxation to about 5%. The high strength polyethylene fibre is quite resistant to repeated axial loading, even if the loading is partly in compression as in bending fatigue. Because of the low friction coefficient and good abrasion resistance, internal abrasion is usually negligible.

The relatively low melting temperature makes the fibre sensitive to warming-up due to hysteresis losses. This process causes warming of the rope and the balance of energy creation and energy loss to the environment determines whether the rope will stand a long-lasting test. High-speed loading and relaxation may lead to high temperatures, but a thick rope immersed in water may stand the test without any difficulty, as has been shown in, for example, offshore mooring.

In bending fatigue or flex-life testing, a loaded rope is moving over two or three sheaves. In the test with three sheaves, two sheaves bend the rope clockwise, and the middle one counter-clockwise. In this test the fibres and the strands move relative to each other and cause internal abrasion. It is clear that the rope construction has a great influence on the results



3.8 **Bending fatigue of various fibres: cycling over sheave at increasing percentage of break load.**

of this test, but as HPPE fibres have a very high abrasion resistance the test results are comparable with those from commonly used synthetic fibre ropes and far higher than aramids and carbon fibres. See Figures 3.7 and 3.8.

3.4.7 Abrasion resistance

Abrasion resistance is very important in ropes, also in gloves. In many of applications it is at least one of the factors that determines wear and tear and so the service life. The high molecular weight polyethylene used for HPPE fibres is also a well-known engineering plastic. As such it is especially used for its superior wear and abrasion resistance. So it is not surprising that the HPPE fibres also have good abrasion resistance.

3.4.8 Effects of water

Polyethylene is not hygroscopic and does not absorb water. The fibres have a very low porosity, therefore water absorption in the fibre is negligible. However, multifilament yarns used as strands in a rope or in a fabric,

Table 3.4 Resistance of fibres to various chemicals: 6 months immersed at ambient temperature

	HPPE	Aramid
Distilled water	***	***
Sea water	***	***
10% detergent	***	***
Hydrochloric acid (pH = 0)	***	*
Nitric acid (pH = 1)	***	*
Glacial acetic acid	***	***
Ammonium hydroxide	***	**
Sodium hydroxide (pH > 14)	**	*
Petrol	***	***
Kerosene	***	***
Toluene	***	**
Trichloromethane	***	***

*** Unaffected ** slightly affected * seriously affected.

typically have 40% void. Therefore, water can be absorbed between the fibres. If that is not acceptable, water repellent additives should be used.

Polyethylene fibres do not swell, hydrolyse or otherwise degrade in water, seawater or moisture.

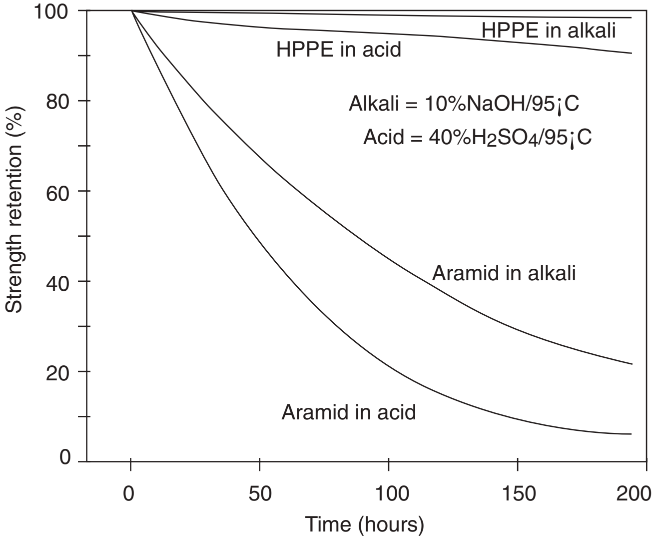
3.4.9 Chemical resistance

HPPE fibres are produced from polyethylene and do not contain any aromatic rings or any amide, hydroxylic or other chemical groups that are susceptible to attack by aggressive agents. The result is that polyethylene and especially highly crystalline, high molecular weight polyethylene is very resistant against chemicals. Table 3.4 gives examples of the effect of chemicals on HPPE fibres, in comparison with aramids. The resistance to acids and alkalis is also very good, see Fig. 3.9.

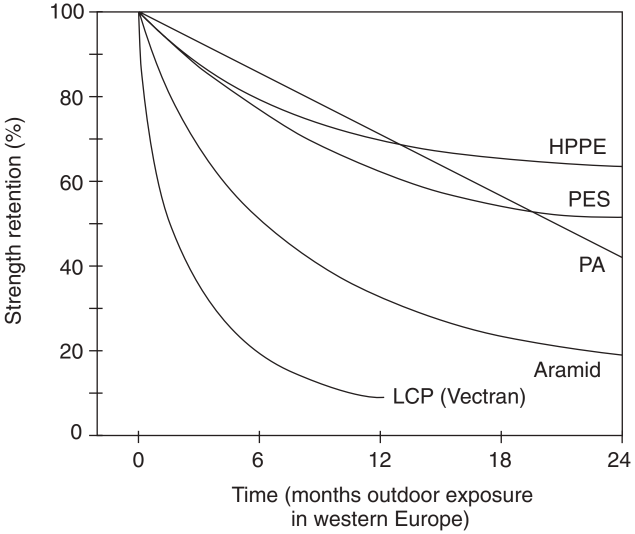
Dyneema and *Spectra* fibres, being of a polyolefinic nature, are sensitive to oxidizing media. In strongly oxidizing media, fibres will lose strength very fast. In normal air the fibre is stable for many years.

3.4.10 Resistance to light and other radiation

Figure 3.10 shows the resistance of HPPE to ultraviolet (UV) light. It is clear that special precautions are not necessary during processing or storage. However light resistance may become limiting when the material is exposed to UV light continuously or for a prolonged time.



3.9 Resistance to acids and alkalis: HPPE *vs* aramid.



3.10 UV resistance of high performance fibres.

Exposure to high energy radiation, as e-beam or gamma radiation, will result in chain scission and a reduction of tenacity. The effect is significant for doses of 100 kGy; however, the fibres retain a useful tenacity up to a dose of 3 MGy.

3.4.11 Electrical properties

Polyethylene is an insulator and has no groups with dipole character. The fibre is characterised by a high resistivity (volume resistivity $>10^{14}\,\Omega\text{m}$), low dielectric constant (2.2) and a very low dielectric loss factor (2×10^{-4}). As-spun yarns contain a small fraction of spin oil of a hydrophilic nature. So, for applications where the electrical properties are important, the spin finish should be removed.

3.4.12 Acoustic properties

As with all mechanical properties, the acoustic properties are strongly anisotropic. In the fibre direction, the sound speed is much higher ($10\text{–}12 \times 10^3$ m/s) than in the transverse direction (2×10^3 m/s). The acoustic impedance, the product of density and transverse sound speed, is near that of water. Mechanical damping losses are significant in both the longitudinal as well in the transverse direction.

3.4.13 Biological resistance

The biological resistance of the fibre is that of high-density polyethylene. The fibre is not sensitive to attack by micro-organisms.

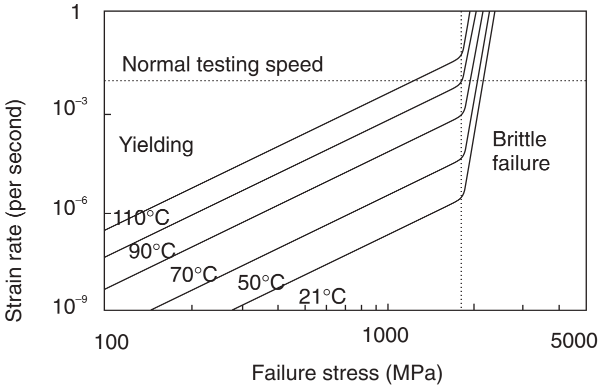
3.4.14 Toxicity

Polyethylene is regarded as biologically inert.

3.4.15 Thermal resistance

Dyneema has a melting point between 144 and 155 °C, depending on the conditions, the higher temperature being measured if the fibre is constrained. The tenacity and modulus decrease at higher temperatures but increase at sub-ambient temperatures. There is no brittle point down to 4 K (–269 °C), so the fibre can be used from cryogenic conditions up to a temperature of 80 to 100 °C. Brief exposure to higher temperatures, but below the melting temperature, will not cause any serious loss of properties.

The mechanical properties are influenced by the temperature and the main reason is thought to be chain slippage, that is polyethylene chains that move relative to each other in the direction of the fibre (Peys *et al.*[6]) (see Fig. 3.11). Normally the testing of tenacity and modulus is done around 1% per second, so below about 100 °C breakage will always be in the brittle failure range.



3.11 Effect of temperature on the failure stress of *Dyneema*.

3.4.16 Fire properties

HPPE fibres and products have been tested to establish the performance in heat and fire. The results are that ignition of HPPE fibres is normal and acceptable under most conditions. The emission of toxic gases in fire was studied and, as polyethylene contains only carbon and hydrogen and no nitrogen or other hazardous chemical elements, toxicity of the gases is relatively low.

Fire properties are far more complicated than indicated by just the LOI (limiting oxygen index). Like most polymeric and organic materials, *Dyneema* and *Spectra* fibres have a LOI index lower than 20, which simply means that they can burn in atmospheric conditions. A number of tests were conducted to specify the fire properties.

- Flammability test, Federal Motor Vehicle Safety Standard (FMVSS 302).[7]
  A US standard that is used in the automobile industry. This test on a horizontal sample qualifies it as being self-extinguishing.
- Flammability test, Federal Aviation Regulation (FAR) 25.853 b.[8]
  Also a US standard and in use with the aviation industry. In this test the specimen is mounted vertically. As in the preceding test, the fabric shrinks away from the flame and no ignition occurs. No dripping was recorded.
- DIN 4102, 'Behaviour of building materials and components in fire'.[9]
  A German standard that was first designed to establish the fire properties of building products but that is now more generally used. Also here, no dripping of material occurred. The samples passed the DIN 4102 B2 test.

All polymeric materials are combustible and their behaviour when exposed to heat and fire differs less than it often seems to do. Thermoplastics normally melt first, then decompose, and in the end the gases from the decomposition start burning. Thermosets do not melt but start decomposing. The decomposition temperature and the ignition temperature of the gases are usually in the same range as for thermoplastic polymers. HPPE fibres are polyethylene, a thermoplastic material that melts at about 150 °C and decomposes over 300 °C. Aramid fibres are thermosets, there is no melting point and gas emission starts at about 400 °C.

The toxicity of the gases in a fire depends on:

- The composition of the substrate; if the material contains nitrogen, sulphur or chlorine (or any other halogen), such as polyamides and aramids, the gases are always toxic. If these chemical elements are not present, toxicity fully depends on the conditions in the fire.
- Given the composition, the conditions in the fire are by far the main parameters for the development of toxic gases. The local temperature and oxygen concentration determine which gases are produced.

3.4.17 Shrinkage

The fibre is characterised by high molecular extension of the molecules. When given sufficient mobility, the chains will contract in order to return to the thermodynamically preferred coiled conformation. Shrinkage is negligible below 100 °C, and will occur mainly between 120 °C and 140 °C. If the fibre is constrained, it will develop significant shrinkage forces (up to approximately 0.1 N/tex).

3.4.18 Properties summary

Table 3.5 gives an overview of the chemical and physical properties of HPPE.

3.5 Yarn and fabric processing

3.5.1 General precautions

Processing of *Dyneema* and *Spectra* yarns is not difficult, but to keep tenacity and modulus as high as possible some precautions should be taken:

- The use of ceramic guides, preferably rolling, is advised. Contact points should have a durable matt surface (so-called orange skin). This can be secured through the use of ceramic materials or by inchromising metal contact points. Contact points should be without burrs or grooves.
- Sharp angles and high tensions during processing should be avoided.

Table 3.5 Overview of chemical and physical properties of HPPE

Water and chemicals	
Moisture regain	zero
Attack by water	none
Resistance to acids	excellent
Resistance to alkalis	excellent
Resistance to most chemicals	excellent
Resistance to UV light	very good
Thermal	
Melting point	144–155 °C
Boiling water shrinkage	<1%
Thermal conductivity (along fibre axis)	20 W/mK
Thermal expansion coefficient	-12×10^{-6} per K
Electrical	
Resistance	$>10^{14}$ Ohm
Dielectric strength	900 kV/cm
Dielectric constant (22 °C, 10 GHz)	2.25
Loss tangent	2×10^{-4}
Mechanical	
Axial tensile strength	3 GPa
Axial tensile modulus	100 GPa
Creep (22 °C, 20% load)	1×10^{-2} % per day
Axial compressive strength	0.1 GPa
Axial compressive modulus	100 GPa
Transverse tensile strength	0.03 GPa
Transverse modulus	3 GPa

3.5.2 Yarn processing, blends and fusing

All the HPPE fibres are produced as filament yarn and by the far largest part is used as such. Twisting and twining can be done using standard machinery. Table 3.6 shows the influence of twist on the tenacity. The k-factor is highly independent of the yarn titre and is calculated as:

$$k = (\text{dtex/density})^{1/2} \cdot (\text{turns/meter})/3025$$

HPPE fibres can be cut to long or short staple or can be stretch broken. Short staple fibre can be processed using open-end and ring spinning, the latter producing spun yarn with superior properties. Long staple fibre and stretch broken fibres can be spun on wool spinning equipment (three cylinder spinning). Both short and long fibres can be combined with other fibres to form blended yarns.

A large number of fibre blends has been produced for different applications but most for cut protection. Both filament yarns and long and short staple can be used.

Table 3.6 The *k*-factor and tenacity

k-factor	Tenacity (%)
0	100
0.57	104
0.85	104
1.13	96
1.70	85
2.83	65

A unique property of high-strength polyethylene fibres is the ability to be fused into monofilaments or tapes. Both *Dyneema* and *Spectra* have been used to fuse the multifilament yarn to a monofilament. These monofilaments are in use in sport fishing lines and are under test in filter cloth.

3.5.3 Dyeing

Owing to their chemical inertness and high crystallinity, dyeing high-strength polyethylene fibres is extremely difficult. A limited success has been demonstrated by using advanced technology, for example dyeing in subcritical carbon dioxide.

3.5.4 Weaving

When weaving *Spectra* and *Dyneema* yarns, the main concern is to minimize the loss of tenacity and modulus. The areal density and the construction of the fabric influence the performance of the final product. In Table 3.7, a first indication is given of the yarns and fabrics used in a number of applications.

3.5.5 Knitting

Knitting of HPPE yarns does not require any special equipment. Filament yarns can be used in all available grades and deniers. HPPE filament yarn has been used as such for 100% *Dyneema* or *Spectra* fabric. The filament yarn is also knitted in combination with cotton to improve wearing comfort or to diminish the performance where 100% would give better-than-needed results.

In cut-resistant clothing, 100% HPPE filament yarns are used and combinations of HPPE filament with other (filament) yarns. *Dyneema* filament yarns are stretch broken and then spun with a great range of other fibres to obtain an ‘engineered’ yarn with well-defined properties.

Table 3.7 Woven fabric styles and applications

Ballistic vests
*_Dyneema SK76_
*_Spectra 1000_ and _2000_
*very tight fabrics

Composite ballistic armour
*_Dyneema SK76_
*_Spectra 1000_
*pliable fabrics (satins)

Protective clothing
*_Dyneema SK60, SK65_ or _SK75_
*_Spectra 900_ or _1000_
*knitted or woven fabrics

Composite reinforcement
*_Dyneema SK60, SK65_ or _SK75_
*_Spectra 1000_
*corona or plasma-treated yarn or fabric
*open fabrics
*hybrids with glass or carbon fibres

3.5.6 Ropemaking

In ropemaking, whatever the rope construction, the key to good performance is to keep the HPPE fibres under constant tension and to avoid differences in path length during processing. The contact points are very important: these should be hard, preferably rolling and certainly not worn-out. These requirements have to do with the high tenacity and the low elongation. The fibre as such, however, is flexible and very easy to process.

Double braids with HPPE or polyester in the outer layer are in common use. HPPE ropes can be heatset to remove the extra elongation that is introduced during the production of the ropes and to increase the strength. This action results in an improved orientation of the HPPE fibres in the ropes. Heatsetting HPPE ropes or twines must always be done under tension.

With HPPE, the double-braided rope construction is mostly used for flexible, dynamic loaded ropes up to 16 mm diameter. The 4 × 2 plaited and 12 × 1 braided ropes are used in far higher diameters and breaking strengths.

Laid ropes have a higher breaking strength but are less flexible. In highly dynamic loaded applications (much bending, changing tension loads, much handling) braided or plaited constructions are often preferred. There are no special problems with HPPE fibres in this application. The ropes are often produced with a braided cover to prevent damage to the load bearing strands.

3.12 Construction of *Dyneema UD* and *Spectra Shield*.

3.5.7 Netting

Normally fishing nets, safety nets, etc. are made by knotting braided HPPE twines to form net panels that are used to build, for example, a trawl net. Single knots in HPPE nets may lead to knot slippage owing to the slippery nature of the fibres so double knots are advised. In knotless nets (Raschel and Nichimo), the panels are produced directly from the yarn and twines are not made first. Heatsetting is common practice with HPPE nets for the same reasons as with ropes, but also to improve fixation of the knots.

3.5.8 Nonwovens

Dyneema UD and *Spectra Shield* are non-wovens, but not of the conventional types. They are made of unidirectional layers, in which the yarns are not woven but lie parallel to each other and are bonded by various thermoplastic matrices, Fig. 3.12. This construction is used in ballistic protection against bullets (police vests, lightweight armour panels) as this gives a far better protection at the same weight than fabrics. This system is patented and *Dyneema UD* and *Spectra Shield* are only produced by licensed companies.

Dyneema Fraglight is a needle felt non-woven, produced from staple fibre, that is used, for example in military vest, for the protection against fragments from exploding grenades and bombs.

3.5.9 Composites and laminates

In non-ballistic composites, HPPE fibres are mainly used to improve the impact resistance and the energy absorption of glass or carbon fibre reinforced products. Woven fabrics or hybrid fabrics with glass or carbon can be used and the fibre or the fabric can be corona or plasma treated to improve the adhesion of the matrix to the fibre. The matrix material is normally an epoxy or a polyester resin. The only basic limitation here is that the curing temperature should not exceed 140 °C.

In composites used for ballistic protection, such as helmets and lightweight armour panels, only the ballistic fibre types are used. Both fabrics and the unidirectional products are used with thermoset and thermoplastic matrix systems. The fibre content is normally far higher than with non-ballistic composites.

Dyneema and *Spectra* are well suited for use in flexible composites or laminates. Most common use is in laminated sails using a scrim or an open fabric and polyester film.

3.6 Applications

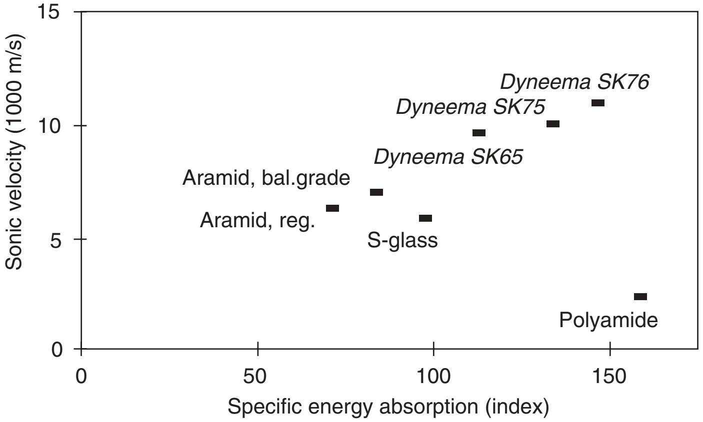
3.6.1 Ballistic protection

HPPE fibres have a high energy absorption at break and, owing to the low weight, the specific energy absorption is also very high. This opens up opportunities for these fibres in applications that need a combination of low weight and protection against mechanical threats.

Most important in ballistic protection are the mechanisms of energy absorption at ballistic speeds. The tenacity and elongation to break determine the amount of energy that can be absorbed by an amount of fibres. The specific modulus determines the sonic velocity in the fibre and that indicates the area of the fabric that is involved in stopping the projectile. Figure 3.13 shows the specific energy absorption and the sonic velocity of fibres: the primary factors that determine the weight needed to stop a projectile.

Against most ballistic threats, unidirectional layered HPPE constructions *Dyneema UD* and *Spectra Shield* give the best protection: this means protection at the lowest weight. The theory behind the unidirectional layer construction is that at ballistic impact of a fabric, the spread of energy in the fibres is hindered by reflections of the shock waves at the crossover points of the yarns. In the unidirectional construction, this is far less and a larger part of the sheet is involved in the absorption of energy.

HPPE fibres are used both in ‘soft’ and ‘hard’ ballistic protection. Soft ballistic protection is used in flexible vests for the police and military, and protects against handgun ammunition. In police vests the unidirectional form is used as such or in combinations with woven fabric from low titre HPPE or other fibres. Helmets and lightweight panels are hard armour. The military helmets protect against fragments from bombs and grenades; the armour panels can also protect against highly penetrating military rifle



3.13 **Energy absorption and sonic velocity in ballistic fibres.**

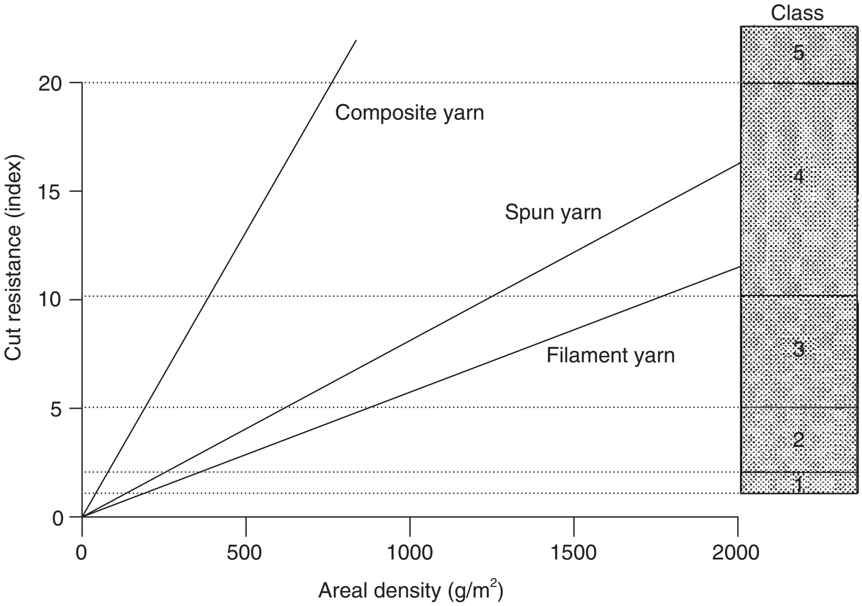
ammunition and can be incorporated in vests and also in civil cars and lightweight (military) vehicles.

3.6.2 Cut and puncture resistance

The protecting properties of HPPE fibres can be exploited not only in ballistic applications, but also in protection against cuts and puncture. Woven fabrics and knitwear give a very good protection in, for example cut-resistant gloves, fencing suits and chain-saw hoses. In cut resistance the best protection is achieved when high-performance fibres are combined with stainless steel or glass fibres. Theory does not give a full explanation of this effect but in practice most gloves are knitted using yarns formed from a combination of HPPE and other fibres: so-called engineered yarns. In engineered yarns, HPPE filament or staple fibre and various other yarns such as stainless steel, glass, polyamide, polyester and cotton are combined, partly to improve the cut resistance, partly to improve, for example, wearing comfort. Figure 3.14 shows the cut-resistance according to the European standard EN 388 (1994).[10] *Dyneema* engineered yarns meet the requirements of the highest Class 5.

Puncture resistance depends on both the fibre properties and the resistance of the fabric construction against penetration between the yarns. A normal knitted HPPE fabric can easily stand the test for fencing suits against penetration by the blunted weapon, but an ice pick will easily penetrate such a fabric.

The low moisture sensitivity and good chemical resistance of HPPE fibres guarantee high durability in the wash-and-wear cycles of protective clothing.



3.14 Cut-resistance according to European Standard EN 388.

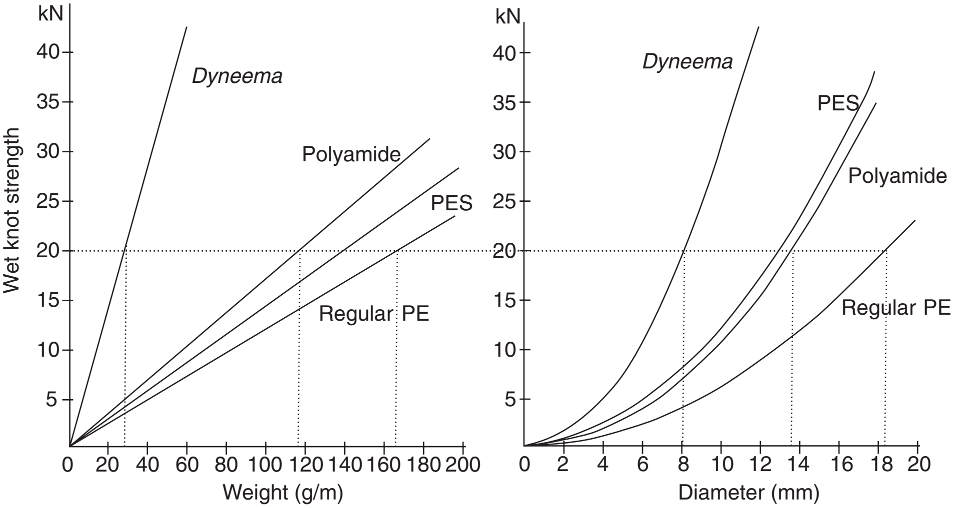
3.6.3 Low-speed impact

In composites, HPPE fibres can absorb the impact energy that would otherwise destroy the brittle reinforcing glass or carbon fibres. In addition, the use of HPPE affords great weight savings. In motor helmets, for instance, a weight saving of 300–400 g has been realized, down to 40% of the original shell weight. Even in combinations with wood laminates for boat hulls for instance, HPPE fibres can strongly improve impact resistance.

3.6.4 Twines and nets

An HPPE fibre is an ideal material for use in a marine environment. Its density is slightly less than 1, so it is virtually weightless in water and floats. The fibre is strong and does not loose its tenacity in water, it does not rot and is not affected by UV light or seawater. So it is not surprising that ropes, twines and nets were among the first products to be made of these fibres.

Most important applications of smaller cords are in halyards, twines for nets and the very thin lines used for angling. Halyards normally have a double braid construction with a braided load-bearing core and a coloured polyester cover. On a weight basis, the halyards with a HPPE core are by far the strongest on the market. Elongation is only slightly higher than that



3.15 Wet knot strength of various twines in fishing nets.

of wire rope so that HPPE halyards guarantee accurate and stable positioning of the sails. In long-distance sailing contests, it was confirmed that the ropes are reliable and durable, and HPPE halyards are now the standard in these contests.

Very thin, ultra-strong braided HPPE angling lines were a major change in sport fishing after many years of polyamide monofilament. The braided line was followed by a fused HPPE line with monofilament characteristics. Not only is a HPPE line far stronger than polyamide at the same diameter but owing to the low elongation the angler has far more 'contact' with the fish.

The reduction in weight and diameter of ropes and twines in trawl nets opens up new opportunities for the design of more efficient nets. The drag resistance of the net in water can be reduced by as much as 40% per square metre net opening. This benefit can be utilized to save energy on trawling or to use larger nets with a larger mouth opening for the same ship with the same horsepower. Fishing efficiency can be increased by 80% in this way. Figure 3.15 shows the wet knot strength of braided twines that are used in fishing nets. The wet knot strength is the lowest strength in netting and is taken as the design criterion in nets.

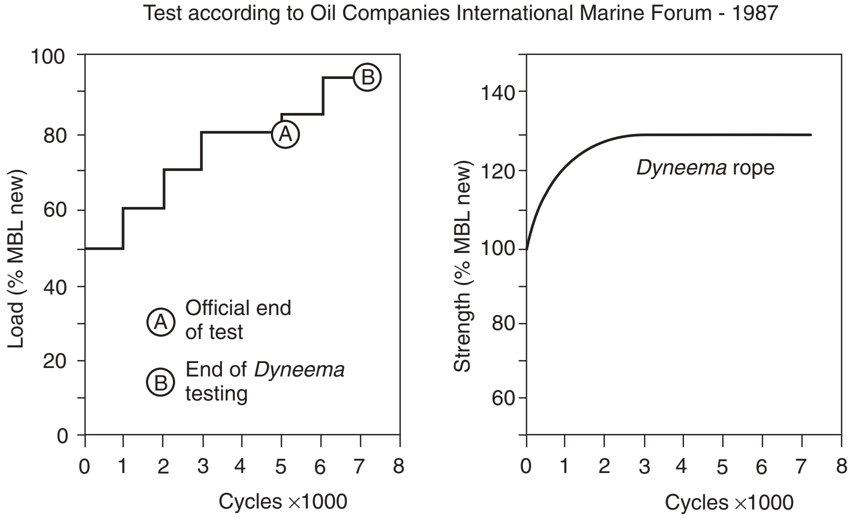
Of course, the weight of fishing gear can also be reduced by using HPPE in the wing lines, jompers and gilson lines, etc. Alternatively, using the same rope diameter but with a rope made from HPPE in the construction of the net or in the cod-end, the risk of breakage, and so the loss of the catch, can be reduced.

3.6.5 Ropes

The low weight and high strength of HPPE fibres make it possible to produce heavy-duty ropes with very special characteristics. HPPE ropes float on water, are flexible and have a low elongation. Thus, they are very easy to handle. Abrasion resistance and fatigue are good to any standard, which is why HPPE ropes last much longer than other ropes. In a matrix in Table 3.8, the different ropes constructions and different types of loading are shown with an indication of the use of HPPE fibres.

Dyneema ropes were tested as to their suitability for offshore applications according to the thousand cycles load level (TCLL) test of the Oil Companies International Marine Forum (OCIMF).[11] The TCLL test is an accelerated fatigue test in which the rope is loaded and unloaded 1000 times with loads of 50%, 60%, etc. of the breaking load. The residual strength is determined after testing at 80% if the rope did not break during testing. In tests carried out on the *Dyneema* ropes, the increasing strength of these ropes frustrated the testing procedure. The testing was continued to 95% of the breaking load and then the residual strength was determined at 130% of the initial breaking load (see Fig. 3.16.).

Figures 3.17 and 3.18 show the strength of a number of ropes versus diameter and weight. The low weight and low elongation of a HPPE rope can be used to reduce the effects of backlash on breakage. In some applications it is advantageous that, at the same strength, a HPPR rope and a wire rope

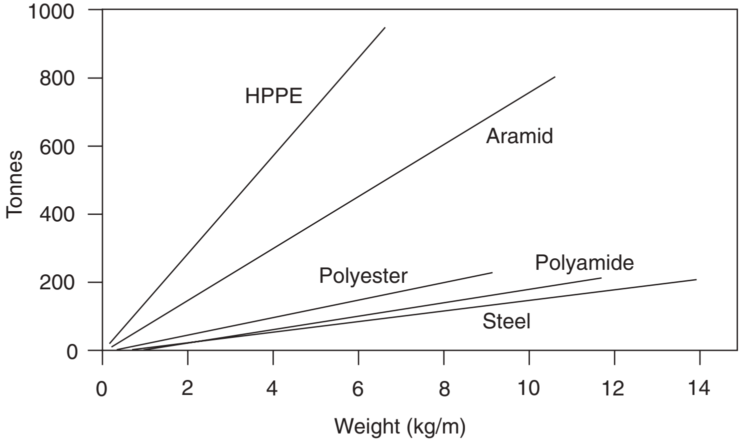

Test according to Oil Companies International Marine Forum - 1987

3.16 The thousand cycles load level (TCLL) test. MBL = minimum breaking load.

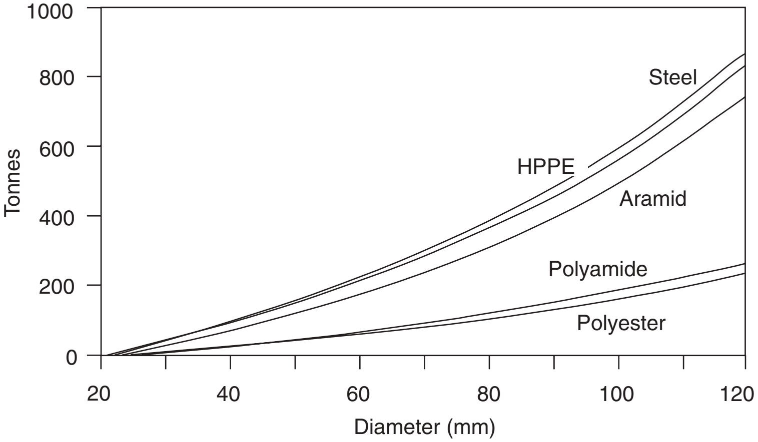
Table 3.8 Constructions and applications of HPPE ropes

Demand	Static loading		Slowly increased loading				Shock loading		Load in bending	
Application	guys	fasten	mooring	tug	fishnet rope	nets	safety	mountaineer	changing	static
									hoisting	stretch
Construction										
Laid, 3 strand			++	+	++				+	
Laid, 4 strand			+						+	
Braided		+	+		++	++			++	
Double braid		+	+	++	+				++	
12 strand braided				++						
Parallel	+									+

+ in common use, ++ recommended.



3.17 Breaking strength *vs* weight of various laid ropes.



3.18 Breaking strength *vs* diameter of various laid ropes.

have about the same diameter. Heavy-duty HPPE ropes are used on tugboats for towing, on ferries and other sea-going vessels for mooring, for mooring offshore platforms and for a large number of auxiliary applications in the offshore industry.

3.6.6 Other applications

Low-stretch sails that last a long time and that can be used and stored repeatedly without loss of properties are now possible by using HPPE fibres. Excellent class sails are now available not only for the professionals, but also for recreational sailors who want their sails to last longer than one season. HPPE sails are mainly used for the main sail and foresails. Low weight and high strength are very important in these applications.

Both *Dyneema* and *Spectra* have been used to reinforce laminates that are used in balloons for stratospheric exploration and in balloons used for load-bearing applications at lower altitudes.

Hoisting slings can be made from a rope, from narrow fabric or can be laid from yarns or twines. HPPE is used in all types. Weight saving is normally not the first reason to choose this material, service life is more important.

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