Polyethylene vs. para-aramid fibers

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The producers of the high-performance polyethylene (PE) and aramid fibers claim the most fantastic properties such as stronger than steel. These fibers compete in the market in the areas of cut-resistant gloves, ropes and ballistics. In this article the pros and cons are critically evaluated to aid the reader in understanding the facts. In order to properly understand the difference between aramid and PE fibers, some process development aspects will be discussed first.

Development of aramid fibers

Carothers, the inventor of polyamides (nylons) in the 1930s, already postulated the prerequisites for a high strength and high modulus polymeric fiber viz: long chain polymer molecules arranged in parallel with the fiber axis. All synthetic polymers, however, like polyethylene (PE), polyamides (PA), polyesters (PET) etc. are flexible polymer molecules which can adopt any conformation (shape) and e.g. in the molten state are highly entangled like cooked spaghetti. How is it possible to get these chains together aligned parallel in a fiber? At DuPont in the 1960s they start to explore rigid polymer chain molecules (uncooked spaghetti) which should be much easier to align in a fiber. The polymer PPTA (poly-para-phenylene-terephthalamide) became the base material for the Kevlar fiber (Fig. 1). To synthesize PPTA, notably in a plant, is complex, the reaction between the monomers is very fast and the polymer 'solution' produced in the reactor cannot be used as the spinning dope. PPTA has to be recovered and re-dissolved in a suitable solvent and PPTA dissolves in concentrated sulfuric acid but the solution-viscosity is too high. Kwolek made a major breakthrough when she discovered that the solution-viscosity went down drastically in the concentration range of 15-20 % in which the PPTA chains align in domains like logs in a river (Fig. 1). These liquid crystalline (nematic) solutions of PPTA in sulfuric acid are spun with an airgap into water. Upon entering the water phase sulfuric acid dissolves in the water phase and the PPTA molecules become aligned parallel to the fiber axis and after some heat setting further down the line the fiber is ready for use.

In 1970 Akzo Nobel in The Netherlands entered the field of aramid fibers. A major patent issue started which was settled partly based on the fact that the solvent HMTP used by DuPont proved to be carcinogenic whereas Akzo Nobel found a unique solvent combination, NMP + calcium chloride, and Twaron fiber was born. Teijin took over the business in 2001. Later, in 2015, DuPont and Kolon (South Korea) clashed about industrial espionage which was settled for some US$ 350 million. Currently DuPont and Teijin have >70 % market share whereas other companies like Kolon, Hyosung (South Korea) and Chinese companies come up. The total production volume nowadays is approaching 100,000 tons/year.

Development of polyethylene fibers

Melt-spinning

Melt-spinning of linear PE (HDPE) combined with hot-drawing of the as-spun fibers was pioneered by the late Prof. Ian Ward at Leeds University/UK in the 1970s and for some time commercialized by SNIA (Italy), as Tenfor. At present melt-spun fibers are pro-

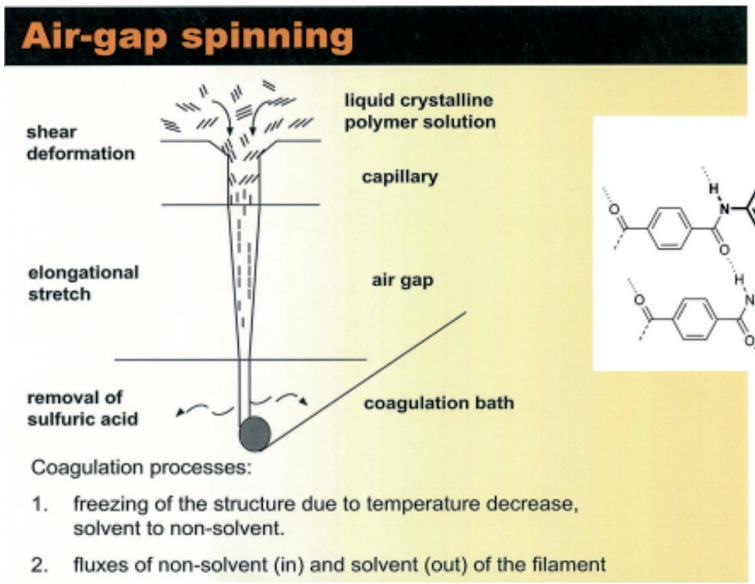


Fig. 1
Aramid fiber spinning, insert structure PPTA molecule

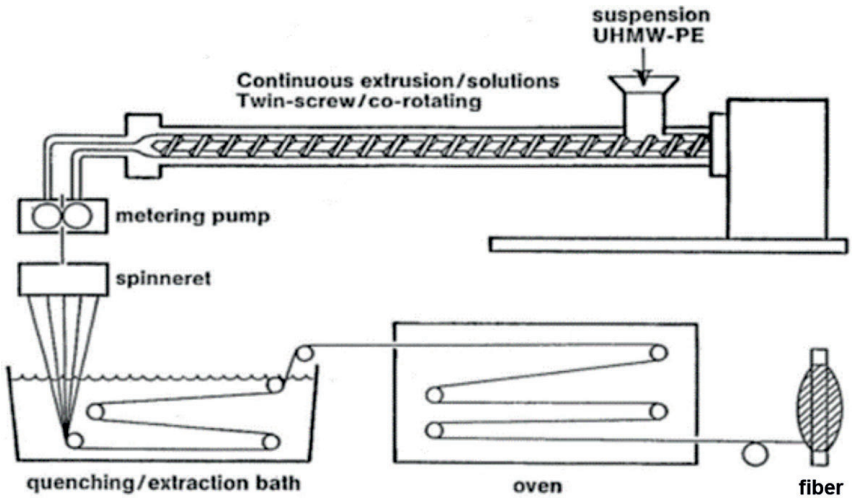


Fig. 2
Schematics Dyneema process. A suspension of UHMWPE in decalin, approx. 10%, is fed to a co-rotating twin-screw-extruder in which the solution is made. The as-spun filaments are quenched in a water bath and subsequently drawn in an oven with simultaneous solvent removal via evaporation.

duced by Toyobo (Japan), as Tsunooga, and Huvis (South Korea), as Duraron, possessing tenacities up to 1.5 GPa and E-moduli of approx. 70 GPa. These numbers are impressive but far below theoretical predictions as discussed below.

Predictions about ultimate strength of PE fibers

Calculations show that a single fully stretched PE molecule breaks at 20 GPa with a corresponding E-modulus of 180 GPa, close to steel (200 GPa). However, these calculations are far from reality because in practice finite polymer chains of at most 10 µm in length when fully stretched (extended) are being dealt with. Consequently, in testing a PE fiber the response will depend on stress transfer between the chains with only weak Van der Waals forces. Therefore, very long chains are needed to generate a sufficient amount of lateral interaction (friction) between the individual molecules. Melt-spun PE fibers are based on low molecular weight PE (approx. 100,000 g/mole) and a much higher molecular weight is needed. Aramid fibers, on the other hand, have stronger interchain hydrogen bonding and a molar mass of some 50,000 g/mole is sufficient to generate the fiber properties.

Solution (gel)-spinning of UHMWPE

Polyethylene grades are available possessing a molar mass > 3 million g/mole, so-called ultra-high-molecular-weight polyethylene (UHMWPE). The major drawback of UHMWPE that it is not processable using standard techniques like screw-extrusion due to the prohibitive high melt-viscosity. A straightforward way to facilitate processing is to make use of a solvent and in the fiber world solvents are used in the well-known dry-spinning and wet-spinning technologies.
In the 1980s at DSM in The Netherlands, solution-spinning of UHMWPE was explored. UHMWPE was dissolved in the solvent decalin at very low concentration, approx. 1%, and spun into fibers. The as-spun fibers were stretched afterwards at elevated temperatures whereby the solvent evaporated. Fibers with a tensile strength > 3 GPa (30 cN/dtex) and a corresponding E-modulus (stiffness) of >100 GPa (1,000 cN/dtex) could be obtained. This observation was not surprising initially because it is well-known in the art that in a solution polymer chains become separated, dis-entangled, resulting in a lower viscosity making the intractable UHMWPE processable. During subsequent drawing of the as-spun fibers the solvent acts as a plasticizer to facilitate the alignment of the long polymer chains in the fiber. What came as a surprise is that the as-spun fibers were still ultra-drawable after removal of the solvent prior to drawing. Apparently, upon solidification of the as-spun fiber in the water quench bath, a favorable topology of the polymer chains is achieved making ultra-drawing and chain-alignment feasible [1]. The concept of the so-called dis-entangled state was coined. A detailed discussion about the morphology/structure of the dis-entangled state is beyond the scope of this article and the reader is referred to [2].
At that time, DSM was not a fiber producer and Akzo Nobel – also headquartered in The Netherlands – was not interested in what they nicknamed a 'candlewax' fiber. Due to interest from Toyobo (Japan) and Allied Spectra (now Honeywell) (USA) the project survived and the Dyneema fiber was born. Nowadays DSM is the leading producer with Dyneema, followed by Honeywell (Spectra) and Toyobo (Izanas) and many Chinese companies.

Chineema

Solution-spinning of UHMWPE is a simple process, consequently easy to copy, and nowadays there are numerous Chinese PE fiber producers, close to 40 at the time of writing, which are referred to as Chineema. Instead of decalin, the Chinese producers almost exclusively use paraffin-oil, which is a less volatile and less flammable solvent but cannot be removed by evaporation during drawing, and so has to be extracted and recovered as shown in Fig. 3.

Fig. 3
Chineema factory – The extruded PE filaments containing ~10% of UHMWPE are collected in boxes with a perforated bottom (left). Upon storage (1 or 2 days) some paraffin-oil will 'sweat-out' (syneresis) and can be re-used directly. The semi-dry filaments are subsequently extracted (heptane) and drawn in a series of heated ovens.

Solvent-free processing of UHMWPE into high-performance tapes

The so-called dis-entangled state which can be obtained by dissolving UHMWPE followed by gelation (crystallization) can also be achieved nowadays during polymerization in the reactor. During polymerization of UHMWPE the polymer chains grow away from the catalytic sites and if these sites are sufficiently separated the growing chains hardly entangle and hence dis-entangled UHMWPE reactor powder is obtained [2]. These powders can be solely processed in the solid state by consolidating the UHMWPE powder into a sheet using a belt-press, followed by calendaring to make the sheets thinner and subsequent (slow) ultra-drawing close to but below the melting temperature. The ultra-drawn sheets are slitted into small tapes. Currently; Teijin Aramid (Endumax) and DuPont (Tensylon) produce these high-performance tapes. DSM produced the BT10 tape but seems to have stopped and is now pre-marketing a better version with higher strength. Details are not yet in the public domain.

Are aramid and PE fibers really stronger than steel?

Producers of aramid and PE fibers claim that their fibers are stronger than steel (PE). The strength of aramid fibers goes currently up to 3.5 GPa and E-moduli close to 150 GPa. (UHMW)-PE fibers nowadays possess a tensile strength in the range of 3->4 GPa and corresponding E-moduli in the range of 130-160 GPa. The UHMWPE tapes possess a very high E-modulus approaching 200 GPa and the strength obtained at lab scale is >4 GPa but commercial grades like Endumax have a much lower strength, <2.5 GPa.

Steel possesses a stiffness of approx. 200 GPa and the yield stress is in the range of 0.25-0.7 GPa. Even more impressive is when the specific values for strength and E-modulus are considered (Fig. 4). The density of a PE fiber is 950 kg/m^3 (lower than water) and of aramid fiber approx. 1,400 kg/m^3 to be compared with steel 7,800 kg/m^3 and glass 2,400 kg/m^3.

Before there is excitement about these data please more information follows below.

Influence of temperature and time

In the world of plastics, the question often is not "if" the material or product fail but "when". In this respect, aramid fibers are an exception. Aramid fibers possess a very high melting temperature estimated to be >500 °C but start to decompose from 400 °C. Increasing temperatures reduce the modulus, tensile strength and break elongation but this becomes a serious issue only at temperatures exceeding 150 °C for extended periods of time. Moreover, the so-called creep, irreversible deformation upon applying a constant load, is no issue with aramid fibers. Aramid fibers subjected to loads in the range of 1-1.5 GPa will survive many decades.

In vast contrast, the properties of PE fibers are highly temperature and time-dependent. The 'melting' temperature of PE fibers is approx. 150 °C (which is in fact no real melting temperature [2]). However, far below the melting temperature, from approx. 70 °C onwards, PE fibers start to lose their properties.

Fig. 5 shows the typical stress-strain curves of respectively aramid and PE fibers. The aramid fibers show a slight convex behavior whereas PE fibers have a concave response and, moreover, with a lower testing speed the curve comes down. At very low testing speeds the PE fiber starts to yield already <0.5 GPa. In a dead-load creep experiment the PE fiber cannot sustain any load and will 'creep' to failure (plastic flow). Scientifically the PE fiber can be considered as a 1-dimensional (1D) liquid albeit with a very high viscosity. At high testing speeds the PE fiber responds as an elastic solid and at very low testing speeds as a liquid. This concept is well-known in polymer rheology (Deborah number).

Applications areas for aramid and PE fibers where they meet and compete

In view of the limited temperature resistance of PE fibers they cannot be used in applications like rubber reinforcement e.g. in tires and conveyer belts but they compete in other areas.

Cut-resistant gloves

Both aramid and PE fibers are used in cut-resistant gloves and provide very good cut resistance which is, however, not related to the high strength and high stiffness. The cut-resistance of melt-spun PE fibers, possessing a 50 % lower strength and stiffness, like Tsunooga, is similar to PE fibers based on UHMWPE like Dyneema and Chineema, showing that the deformation mode experienced in cutting is completely different than upon tensile loading. The market for producing cut-resistant gloves is easy to enter, low-tech, and is nowadays dominated by Chinese producers. DSM upgraded the cut-resistance properties in their Dyneema-Diamond technology by incorporating mineral wool fibers in the PE filaments (the mineral wool fibers blunt the knife) [3].

To make a choice between PE and aramid-based cut-resistant gloves depends on the user applications. For heat protection and flame resistance, the aramid fiber is the winner and will not drip or melt when exposed to open flames. PE fibers possess a remarkable property viz. a high thermal conductivity (40 W/mK) and consequently fabrics based on PE fibers feel cool. Cut-resistant gloves based on UHMWPE have a soft and smooth feel and due to the heat conductivity are very comfortable in a hot climate.

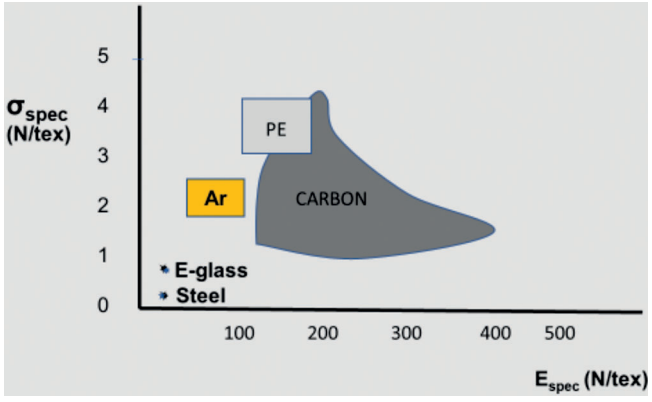


Fig. 4
Specific strength σ_{spec} (N/tex) vs. specific E-modulus (N/tex) at ambient temperatures
Ar = Aramid fibers (N/tex = Gpa/ρ ; ρ in g/cm^3)

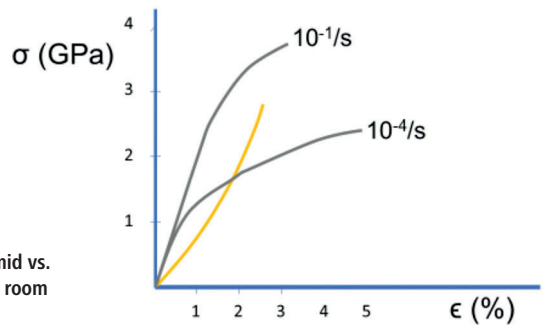


Fig. 5
Stress vs. strain, aramid vs. PE fibers recorded at room temperature

Ropes and cables for mooring and anchoring

The statement above that PE fibers like Dyneema can be considered as 1D liquids sounds quite frightening when considering PE fibers in ropes for mooring vessels or anchoring floating wind turbines to the bottom of the sea. However, the stress on ropes is intermittent for mooring lines and PE cables used for anchoring experience a cyclical stress (motion of the waves). Moreover, some creep will not influence the fiber properties and is currently claimed by DSM as an advantage [4]. The stress on various tension members upon anchoring e.g. wind turbines to the bottom of the sea will equalize after some time which is impossible to realize with steel or aramid cables. Another major advantage is that the density of PE fibers is lower than water, they float on water and have no weight in anchoring and as a bonus, water will not influence the fiber properties, in contrast with aramid fibers. Moreover, at or in deep seas, the temperatures are relatively low and the problem of creep is a minor issue. The problem of creep failure comes at elevated temperatures e.g. in hot climates where temperatures can rise up to 50 °C and in ropes, due to friction even up to 70 °C or even above.

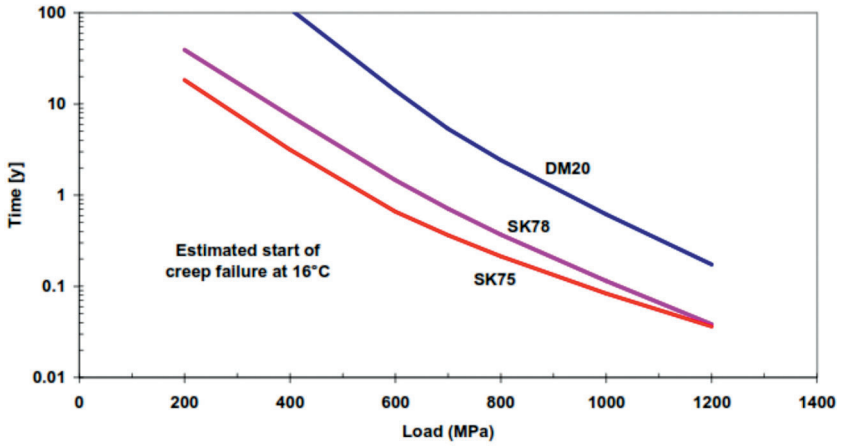
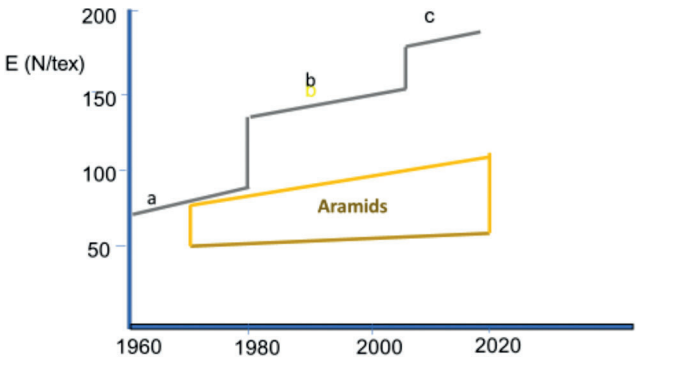


Fig. 6
Creep failure in typical sea water conditions for the standard Dyneema grades SK75 and SK78 vs. the low creep grade DM20

On their website and in several documents Teijin Aramid claims that aramid ropes are much safer than HMPE ropes at elevated temperatures. These statements might be quite true but what is their definition of HMPE? Chineema producers have to buy UHMWPE in the open market from a limited number of suppliers. They use paraffin-oil (white-oil) and to obtain a homogeneous solution in the extruder they operate at high temperatures, up to 300 °C. At these high temperatures UHMWPE degrades and notably the long(er) chain molecules fragment due to mechano-shearing. Surprisingly, the short-term properties are reasonable, viz. a tenacity of 3-3.5 GPa and a corresponding E-modulus of 130-150 GPa but the long(er) term properties like creep and fatigue are inferior.

DSM produces their feedstock UHMWPE in-house and can fine-tune the molecular weight distribution but also the chemical structure e.g. by making UHMWPE copolymers. Moreover, they use decalin as solvent at temperatures operating <200 °C. Currently DSM produces its DM-20 low creep grade based on a UHMWPE copolymer (Fig. 6).

In conclusion HMPE is a generic name but the fibers can be quite different. A detailed discussion about temperature limits in ropes is beyond the scope of this article and the reader is referred to experienced rope and cable makers like Samson, Lankhorst and Fibremax, companies with extensive experience and data bases of both aramid and PE fibers.



a) melt-spinning/drawing PE; b) solution(gel)-spinning UHMW-PE
c) solid-state processing of dis-entangled UHMW-PE

Fig. 7
E-modulus vs. time for aramid and PE fibers and tapes

Ballistics

Kevlar from DuPont became the ultimate fiber for ballistic applications in bullet-resistant vest, helmets and armor and Kevlar became for the general almost synonymous with 'life protection' The ballistic protection of a material depends on its ability to absorb energy locally and on the efficiency and speed of transferring the absorbed energy which is realized in so-called uni-directional (UD)-laminates either as 'soft' inlays or compressed into hard sheets. Kevlar in ballistics can be replaced with Twaron since the fiber properties are the same, however acceptance of new fibers is another issue. Allied Signal (now Honeywell) coined PE fiber for ballistics in the 1990s and currently DSM Dyneema is leading in this area with their SK99 grade possessing a tenacity of >4 GPa.

The advantage of PE fibers is a 50 % lower density and higher strength/stiffness (Fig. 4). In principle, PE tapes like Endumax should perform even better in ballistics. The packing density of tapes in UD-laminates is favorable compared with fibers. The strength, however, is rather limited up to now, approx. 2.5 GPa, and the impact energy is the area under the stress-strain curve. In this respect, in the academic world many papers are published about spider silk 'tougher than Kevlar' which is in fact true but the strain at break is 30 % and soldiers with a low(er) BMI will be fully penetrated. Fibers like aramids and PE can absorb a lot of energy at low strains so causing less 'blunt trauma' (damage).

Future outlook

Ultimate stiffness and strength

Fig. 7 shows the development of the E-modulus in time for aramid and PE fibers (tape). The E-modulus is related to the perfection of chain alignment in fibers. For aramid fibers the E-modulus did not improve significantly despite many efforts made [5]. The chain alignment is obtained in the complex coagulation step and decisive for the E-modulus. Recently, Lustig et al. published an article on 2D aramid fibers based on computer modelling which they claim could be a new generation of aramid fibers [6]. However, modelling is still far from experimental validation.

In the case of PE fibers there are 2 'quantum' jumps and the E-moduli have approached their theoretical limits.
The strength of PE fibers is another issue and many researchers believe that the limits have not been reached. It has been published that the strength will increase with decreasing fiber diameter similar to glass fibers [7]. By extrapolating the fiber diameter to zero an estimated strength of 19 GPa was found in accordance with theory. However, these concepts are basically wrong. It is now generally accepted that failure during tensile loading occurs through chain slippage. An upper limit in strength of 7 GPa seems a realistic value and is already obtained at pilot plant scale but not transferred yet into commercial grades [8].

Green PE and aramid fibers

Bio-based 'green' plastics are making an inroad due the negative image of oil-based plastics. DSM started with bio-based Dyneema using ethylene derived from biomass and/or recycled sources and Teijin Aramid announced to explore bio-based monomers for PPTA. These bio-based fibers are identical to standard fibers and after service life they stay with us forever in the environment. Consequently, recycling is essential as explored e.g. by DSM CirculariTeam). Teijin recycles their Twaron fibers from used car tires which can be used as chopped fibers in brake pads (asbestos replacement).

Hybrid use of fibers

PE fibers are tough but lack compressive strength whereas carbon fibers are brittle but possess very good tensile and off-axis properties. The 2 fibers can be combined in hybrid composites to combine the best of the 2 worlds.
The same applies to combine PE and aramid fibers combining the best of 2 worlds in ballistics, e.g. [9].

Epilogue

The future competition between aramid and PE fibers will depend on the R&D strategy of the new owner of Dyneema. DSM officially announced September 2021 that it will divest its materials activities and will fully focus to become a 'food and feed' company, and therefore, Dyneema is for sale.

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