HOT DRAWING & CHARACTERIZATION OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) FIBERS FOR USE IN ARMOR COMPOSITES

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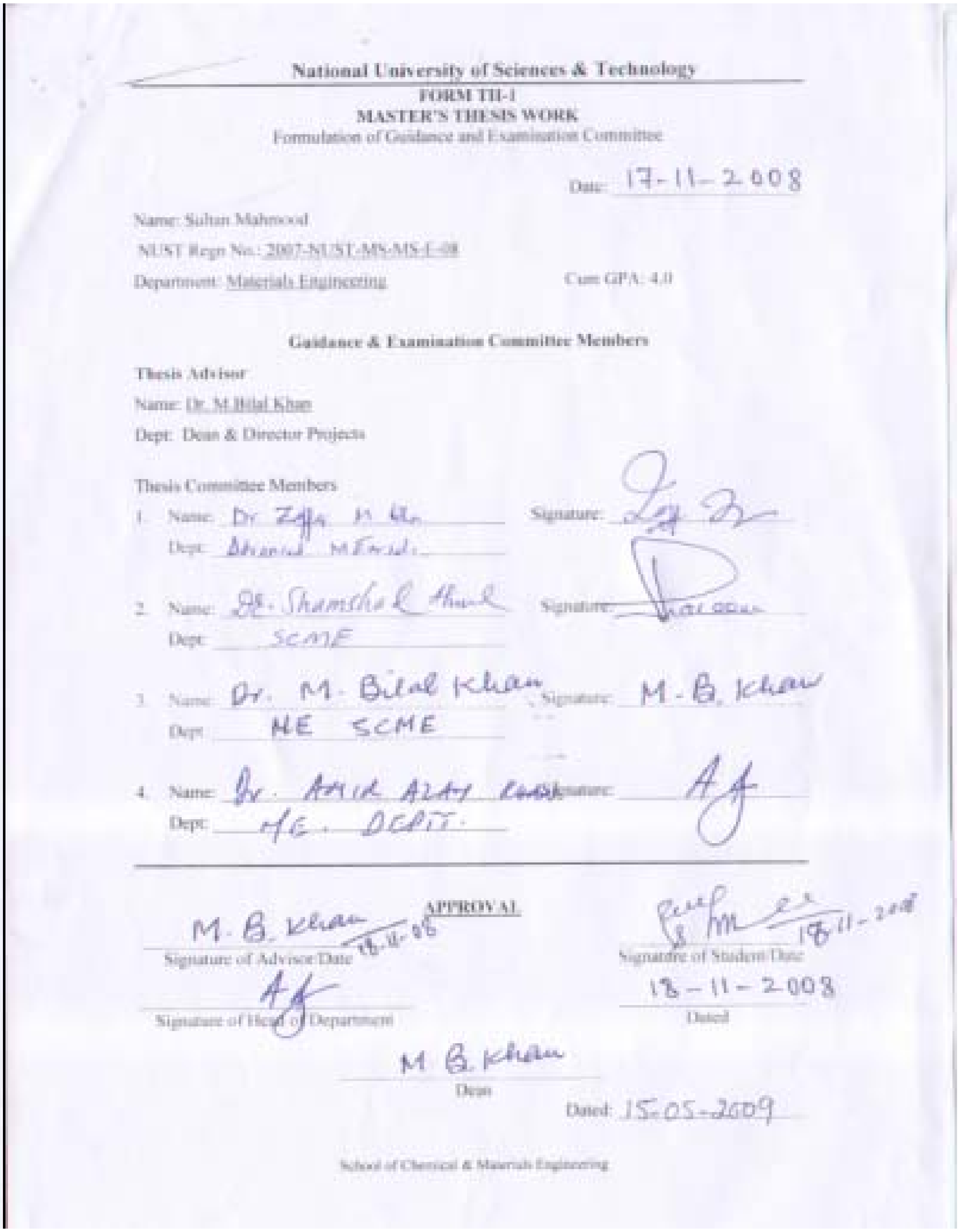

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DEDICATION

Dedicated To My Family

ABSTRACT

Ultra high molecular weight polyethylene (UHMWPE) fibers produced by gel spinning and subsequent hot drawing mechanism have unique, remarkable and promising properties to place them among the strongest and lightest fibers to develop high impact resistant, damage tolerant and light weight armor/ballistic composites.

In this study, hot drawing of gel spun UHMWPE fibers has been conducted to achieve high strength, high modulus fibers by the mechanism of molecular orientation. For this purpose, hot drawing has been carried out in a specially designed hot tube. The influence of as-spun fiber diameter and draw ratio (D.R.) of gel-spun/hot drawn ultrahigh molecular weight polyethylene (UHMWPE) fibers on resultant tensile strength, Young’s modulus, morphology and thermal behavior are investigated using universal testing machine (UTM), scanning electron microscope (SEM) and differential scanning calorimeter (DSC).

The tensile strength and modulus increases almost linearly with the draw ratio due to the greater degree of molecular orientation. SEM micrographs show that at higher draw ratio more fibrillar material is obtained at the expense of lamellae with better chain alignment. It is evident from DSC thermograms that melting endotherm shifts to slightly higher temperature and peak sharpness with increase in draw ratio due to the transformation from amorphous to crystalline phase during the course of hot-drawing process. Similar improvements in the mechanical, morphological and thermal properties of UHMWPE fiber are investigated by employing the as-spun fiber of comparatively smaller diameter. Ultra high molecular weight polyethylene (UHMWPE) fiber is produced with maximum draw ratio of ‘40’ having tensile strength and Young’ modulus of 790 MPa and 5.785 GPa respectively. Whereas, tensile strength and Young’ modulus of un-oriented (compression molded) UHMWPE used for this study has been reported as 28 MPa and 239 MPa respectively.

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In the name of ALLAH, Most Gracious, Most Merciful

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CHAPTER 1

INTRODUCTION

1.1 Light Weight Armor Composites

During the First and the Second World War knowledge about personnel protection was restricted to the use of steel. However, due to the heavy weight of steel armor and lack of flexibility, it was used only on slow moving, heavily armored vehicles. Personnel protection was completely missing. The earliest helmet was a modified metal cap to protect soldiers during the First World War. Flak jackets used for personnel protection during the Vietnam era were heavy, bulky and provided limited protection from high speed projectiles.

Development of lighter and better protective armor is due to the continuous desire to reduce causalities in the battlefield, or during peace keeping and law enforcement. Other factors that play major role in armor development are the reduction of weight of personal protective gear and lessening of the barrier posed by armor during body movement. This reduction in weight reduces the heat burden experienced by the wearer during each activity and ensuring that protective gear does not pose a barrier to the efficient accomplishment of the wearer’s mission [1].

Much of the progress has been recent, fueled by new fiber developments in the traditional aramids and some relative newcomers. And research continues unabated, as threats to military and security forces grow. Now the goal is to stop multiple threats, from knives to high-energy bullets, using an approach that takes advantage of a variety of materials and laminates.

Composites offer two-fold ballistic protection benefit: Fibers resist projectile penetration due to their inherent tensile strength as well as their initial rigidity because they are embedded in and stiffened by the resin matrix. Secondarily, dry fibers absorb energy as they elongate. This gives composites excellent resistance not only to shrapnel but handguns and some high-caliber rifle rounds, as well [2].

1.1.1 High Performance Fibers

Scientists and engineers at various industries, universities and organizations have conducted research work on ballistic materials and their interaction with high speed projectiles. The primary backbones of current light weight, damage tolerant, high impact resistant and durable ballistic composites are the light weight, high performance ballistic fibers.

High performance, man-made ballistic fibers have unique properties which set them apart from other man-made fibers used for industrial applications. The tensile strength and modulus of ballistic fibers are significantly higher. These fibers can be woven on fabric looms more easily than brittle fibers such as fiberglass and graphite fibers. The ballistic fibers also show inherent resistance to a number of chemicals, industrial solvents and lubricants used by automotive and aerospace industries.

Common high performance ballistic fibers are aramid, poly(p-phenylenebenzobisoxazole) (PBO), poly{diimidazo pyridinylene (dihydroxy) phenylene} (M-5) and ultra high molecular weight polyethylene (UHMWPE). Thermoplastic (urethane, synthetic rubber and polyethylene) and thermoset (phenolics and vinylesters) are the resins used most often for lightweight ballistic composites.

1.1.2 Applications

Lightweight, high performance fiber – reinforced armor materials have shown dramatic growth in the last decade. High performance armors are becoming a standard item for militaries and other law enforcement agencies all over the world. Most common applications of lightweight armor are listed below [1]:

Personnel Protection

- Soft flexible vest
- Rigid molded breastplates (with and without ceramic facing)
- Ballistic helmets

Vehicle Armor

- Ground vehicles
- Sea vehicles
- Aircraft and helicopters

1.2 Strong Polymeric Materials

It has been recognized for quite some time that orientation of polymer molecules along a fiber axis may result in strong materials [3]. Although strong materials can be made from metals, polymers have several advantageous properties. A comparison of behavior of different materials in terms of tensile strength-elasticity is illustrated in Fig.1.1 [4]. Polymeric materials have relatively low densities and can be synthesized from substances derived from crude oil or from biological resources. Different approaches to prepare strong polymeric materials have been developed. In case of linear, flexible polyethylene high strength fibers can be made by the surface-growth method [5] and by gel-spinning [6-9]. Fibers from stiff chain aromatic polyamides can be made by spinning and subsequent solidification of liquid crystalline solutions. Polymeric fibers may also serve as precursors for carbon fibers [10,11].

Tensile properties at this level aroused the interest of polymer scientists to investigate the morphology and texture of these fibers as well as the molecular mechanism associated with the oriented crystallization and deformation process. These also stimulated interest in exploring new applications in particular because these crystalline polymeric fibers possess relatively low densities and as a result of that their specific mechanical properties exceed those of steel and glass. The relation between the structure and properties of these materials, on the other hand, is of great scientific interest and has stimulated much research effort. The high strength and moduli of these materials originate from the fact that the macromolecules are oriented in the fiber direction, so that the great strength of covalent bonding along the chain axis is utilized [12].

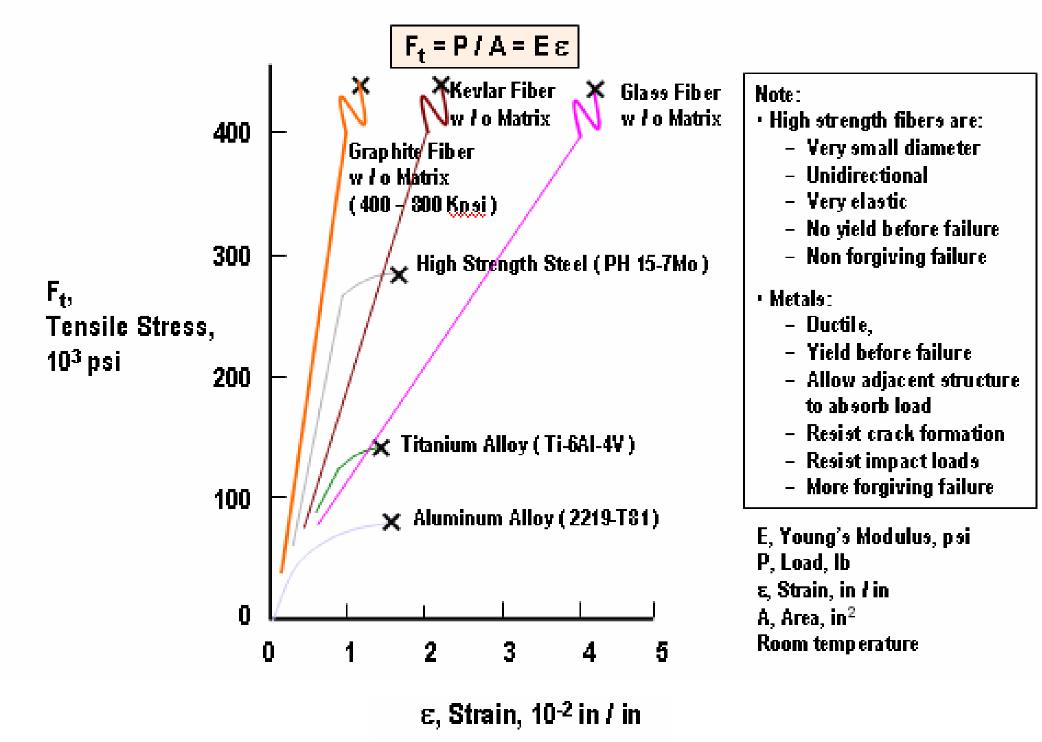


Fig. 1.1 – Tensile strength-elasticity of of different materials

1.3 Orientation of Polymeric Materials

The orientation of polymeric materials has been based upon two general approaches, using either rigid or flexible molecular chains. Rigid chains are processed from the thermotropic or from the lyotropic state, where even low shear stresses are sufficient to cause alignment of the polymer chains in the direction of the flow. Flexible polymers, orientation can be introduced by crystallization from flowing polymer solutions, or by mechanical stretching of the material at elevated temperatures. The process of extending high molecular weight macromolecules is hampered by intermolecular interactions, mainly chain entanglements and polar bonds. Thus highly oriented fibers can be produced by drawing of single crystal atoms and virgin polymers in which little entanglement interactions are present. Since the amount of chain entanglement is substantially reduced upon dissolution of the polymer, polymeric fibers oriented by solution spinning can be drawn to very high ratios, either by draw-down of the spinning thread or in a separate drawing process under controlled conditions. High draw ratios may also be obtained by drawing polymers in their swollen state, where the entanglement density is lower than in the equilibrium melt. In low entangled systems, the maximum draw ratio appears to decrease with increasing chain polarity indicating that, apart from chain entanglements, intermolecular interaction forces (van der Waals and dipole-dipole interactions as well as hydrogen bonding) play an important role in the molecular extension of flexible macromolecules [7,8].

1.4 Ultra High Molecular Weight Polyethylene (UHMWPE) Fibers

In recent years, extensive study has been carried out on highly oriented ultra high molecular weight polyethylene (UHMWPE) fibers and production of ultra high modulus fibers. The production of these fibers were based on attempts to achieve nearly perfect molecular orientation by transforming the chain folded crystalline and amorphous structure of UHMWPE to a highly oriented chain extended structure [13].

1.4.1 Properties and Applications

Apart from their high tensile strength and high modulus, UHMWPE fibers have low density, have an excellent toughness and impact strength, have a very low coefficient of friction, are self-lubricating, and are highly resistant to abrasion (15 times more resistant to abrasion than carbon steel). Their coefficient of friction is significantly lower than that of nylon and acetal. Since UHMWPE does not contain chemical groups (such as esters, amides or hydroxylic groups) that are susceptible to attack from aggressive agents, it is very resistant to water, moisture, most of chemicals, UV radiations, and micro-organisms.

Due to these superior properties such fibers have been widely used in the manufacture of a wide variety of commercial articles, including ballistic vests, ballistic helmets and ballistic vehicle protection, bow strings, climbing equipment, fishing line, spear lines for spearguns, high-performance sails, suspension lines on sport parachutes, rigging in yachting, kites, and kites lines for kites sports. UHMWPE fibers excel as fishing line, as these have less stretch, are more abrasion-resistant, and are thinner than traditional monofilament line [14]. These ultra-high strength fibers are also being looked for by designers of flywheels for energy storage and of ultracentrifuges. Other areas of applications are e.g. microsurgery where the superstrong polyethylene fibers have successfully been employed for cornea transplantations and also for connecting tendons to bone. It is clear that one may conceive of several other new applications and its range will undoubtedly be broadened if the properties of the fibers will be varied by e.g. chemical modification [12]

1.4.2 Production Routes

For the formation of highly oriented fibrous structure and obtaining ultra-high mechanical properties it is essential to employ high draw ratio during the production of UHMWPE fibers. A number of techniques have been tried to achieve high macromolecular orientation and to obtain high strength and high modulus fibers [14]. These techniques include solid state extrusion [15], surface growth techniques [5], melt spinning followed by drawing [18], gel spinning followed by hot drawing [6-9] and drawing of nascent as-polymerized polymers (i.e., obtaining disentangled UHMWPE by direct polymerization in the reactor) [17].

1.4.2.1 Gel Spinning and Hot Drawing

Different fiber processing methods lead to different morphologies and different ultimate properties. However, among these techniques only the gel spinning followed by hot drawing method has been proved to be economically feasible for large scale productions and has been commercialized. In this method, a gel solution of UHMWPE is prepared and spun into fibbers. After shaping the gel solution to a fiber, the solvent should be extracted from it which is done by a solvent of low boiling point. After solvent extraction, the fibers are hot drawn to the maximum draw ratio to achieve a highly oriented structure with high modulus. Considering the fact that fiber production consists of different steps, various parameters influence the final properties of the fibers [6, 7].

1.5 Theoretical Background

Melts and concentrated solutions of flexible polymer molecules are known to exhibit a network like deformation behaviour originating in the presence of numerous molecular entanglements and intertwinings which represent centers of friction for molecular motion. Though some of these may be removed by slippage of molecules past each other during deformation, a considerable number will be trapped during fibrous crystallization. Entanglements, intertwinings, chain ends, loops and other defects are responsible for the lack of tensile strength and modulus in oriented polymers. Therefore fiber of high strength and modulus is produced by minimizing these defects i.e., by using high molecular weight polymers and polymer solutions of low concentrations [18]. High tensile strength and high modulus of hot drawn UHMWPE fibers depend on molecular weight, gel concentration, drawing temperature, fiber diameter and draw ratio [19].

1.6 Objectives

In this study, our objectives are as follows:

- To develop the experimental set up for hot drawing of gel spun UHMWPE fibers.
- To adjust and calculate the drawing conditions such as drawing temperature, residence time and drawing speed.
- To study the stress-strain behavior of UHMWPE fiber with help of tensile testing equipment and investigate the influence of draw stress

or draw ratio and as-spun fiber diameter on the tensile strength and Young's modulus.

- To study the morphology of UHMWPE fibers produced form different initial fiber diameter and hot drawn at various draw ratios, with the help of Scanning Electron Microscope (SEM).
- To investigate the influence of gel spun fiber thickness and degree of stretching on thermal behavior of UHMWPE fibers, using Differential Scanning Calorimetery (DSC).

1.7 References

1. A. Bhatnagar, "Lightweight Ballistic Composites", Woodhaed Publishing. Lim., 1-23, (2006).
2. www. compositesworld.com
3. W.H. Carothers, J.W. Hill, J. Amer, Chem. Soc., **54**, 1579, (1962).
4. A. Kelly, N.H. Macillan, "Strong Solids", 3rd ed., Clarendon Press, (1986)
5. C.E. Meihuizen, A.J. Pennings, A.Zwijnenburg, *US Patent 4,137,394*.
6. P. Smith, P.J. Lemstra, *J.Mater. Sci.*, **15**, 505-514, (1980).
7. I.M. Ward, "*Developments in Oriented Polymers-2"*, Applied Science, 39-77, (1970).
8. J. Smook, A.J. Pennings, *J. Mater.Sci.,* **19**, 31-43, (1984).
9. J.P. Penning, D.J. Dijkstra, A.J. Pennings, *J. Mater. Sci.,* **26**, 4721-4730, (1991).
10. S.L. Kwolek, P.W. Morgan, J.R. Schaefgen, L.W. Gulrich, Macromol., **10**, 1390 (1977).
11. E.E. Watt, B. Perov, "Strong Fibers", Elsevier Science Publishers B.V., (1985).
12. A.J. Pennings, J. Smook, J. de Boer, S. Gogolewski, P.F. van Hutten, Pure & Appi. Chem., **55**, 777—798, (1983).
13. R.B. Seymour, R.S. Porter, "*Manmade Fibers: Their Origin and Development"*, Elsevier Science, 295-310, (1992).
14. R.W Cahn., P. Haasen, E.J. Kramer, "*Materials Science and Technology",* John Wiley, Vol. **18**, Part IV, (1997).
15. *A.* Cifferi, I.M. Ward, "*Ultra-high Modulus Polymers",* Applied Science, 77-115, (1979).
16. J.M. Andrews, I.M. Ward, *J. Mater. Sci.,* **5**, 411-417, (1970).
17. P.Smith, H.D. Chanzy, B.P. Rotzinger, *Polym*er, **30**, 1814-1819, (1989).
18. B. Kalb, A.J. Pennings, Polymer,**1,** 871-876, (1979).
19. J. Smoke, J.C.M. Torfs, A.J. Pnnings, Macromol., **182**, 3351-3359, (1981).

CHAPTER 2

LITERATURE REVIEW

2.1 Polymers

Polymers are classically materials of this century and they have enjoyed an enormous growth in production in past few decades. Considering their low specific mass, 900-1500 kg/m^3, polymers are impending steel in terms of output volume. The scientific name for polymers is synthetic polymers, including their constituent elements: long chain macromolecules consisting of many chemically linked units (poly-meros : many parts).

In contrast to natural polymers (polysaccharides, DNA etc), the chemical structure of present day synthetic polymers is relatively simple. It should be realized that Polymer Science has not matured yet and the creativity of man may eventually produce synthetic polymers whose complexity and functionality are comparable to those of their natural counterparts, present in Man's own body and brains [1]. There is an emerging trend to synthesize so called "specialty polymers" i.e. designing polymeric materials for specific purposes via macromolecular engineering. In view of current activities in this area, both in academe and in industry, it may be expected that in the next decades a whole new class of (initially) low volume, high performance polymers will appear on the market [2].

2.1.1 Classification of polymers

2.1.1.1 Thermosetting Plastics

Thermosetting plastics formed into a permanent shape and cured or "set" by a chemical reaction cannot be remelted and reformed into another shape but degraded or decompose upon being heated to a high temperature. Thus, thermosetting plastics cannot be recycled. The term thermosetting implies that heat (the Greek word for heat is therme) is required to permanently set the plastics. There are, however, many so-called thermosetting plastics which set or cure at room temperature by a chemical reaction only. Most thermosetting plastics consist of a network of carbon atoms covalently bonded together to form a rigid solid. Sometimes nitrogen, oxygen, sulfur, or other atoms are also covalent network structure. Examples of thermosetting plastics are phenolics, epoxy and vinylesters etc. [3].

2.1.1.2 Elastomers

Elastomers are cross-linked rubbery polymers that can be stretched easily to high extensions (e.g. 3 to 10 times of their original dimension) and which rapidly recover their original dimensions when the applied stress is released. This extremely important and useful property is a reflection of their molecular structure in which the network is of low crosslink density. The word rubber, often used in place of elastomer, preferably should be used for describing rubbery polymers which are not cross linked [1].

2.1.1.3 Thermoplastics

Thermoplastics require heat to make them formable and after cooling, retain the shape they were formed into. These materials can be reheated and reformed into new shapes a number of times without significant changes in their properties. Most thermoplastics consist of very long main chains of carbon atoms covalently bonded together. Sometimes nitrogen, oxygen and sulfur atoms are also covalently bonded in the main molecular chain. Pendant atoms or group of atoms are covalently bonded to the main-chain atoms. In thermoplastics the long molecular chains are bonded to each other by secondary bonds. Examples of thermoplastics are polyethylene, polyvinyl chloride, polyproplene, polystyrene and polymethyl methacrylate [3].

2.1.2 Polymeric Fibers

Polymer fibers are a subset of man-made fibers, which are based on synthetic chemicals rather than arising from natural materials by a purely physical process. Such fibers are made from [4]:

- Polyamide nylon,
- PET or PBT polyester
- Phenol-formaldehyde (PF)
- Polyvinyl alcohol fiber (PVOH)
- Polyvinyl chloride fiber (PVC)
- Polyolefins (PP and PE)
- Acrylic polymers, pure polyacrylonitrile PAN fibers are used to make carbon fiber by roasting them in a low oxygen environment.
- Aromatic polyamids (aramids) such as Twaron, Kevlar and Nomex. Polyurethane fiber being used in stretchable garments.
- Polyethylene (PE), eventually with extremely long chains / UHMWPE (e.g. Dyneema or Spectra).

2.2 High Performance Fibers

High performance fibers are engineered for specific end uses that require exceptional strength, heat resistant and/or chemical resistance. They are generally niche products, such as lightweight composite materials for aircraft, ballistic fibers and bullet resistant vest or body armor, protective gear for security personnel, and cut or stab resistant articles. On the lighter sides examples are fishing line, bowstring and marine rope and sail cloth.

2.2.1 Requirements for High Performance Fibers

In order to achieve high performance fiber with exceptional tenacity and modulus properties, there are at least three necessary requirements.

1. The molecule must be highly oriented in the fiber axis direction.
2. The molecular weight or the molecular chain length must be very high.
3. The fiber must be highly crystalline with few defects.

Generally, there are two approaches in manufacturing high performance fibers to meet the above criteria. One can start with a highly oriented but relatively low molecular weight, rigid chain and or rod like polymer (see Fig. 2.1) such as an aramid. This can then be spun into fiber and given a high molecular weight by drawing and/or annealing process. Aramid spinning may be used as an example for this approach.

Fig. 2.1- Random rods of polymers

Fig. 2.2 Random coils of polymers

On the other hand, one can start with an ultra high molecular weight, flexible long chain randomly coiled polymer like ultra high molecular weight polyethylene (UHMWPE) (see Fig. 2.2). Since the ultra high molecular weight polymer can not be melt spun (polymer will decompose before it will flow at the melting temperature), one must spin this polymer with a dilute solution in the range from 2 to 30 % concentration. In this dilute solution, the ultra high molecular weight polymeric chain will ‘uncoil’ and form a network called a gel. By this ‘gel spinning’ method, a long molecular chain xerogel fiber with a loosely connected network can be made. The xerogel fiber can be drawn to a highly oriented, highly crystalline, high performance fiber via specially developed drawing techniques. High performance UHMWPE fibers like Spectra or Dynneema are examples of such fiber.

2.2.2 Classical High Performance fibers

2.2.2.1 Glass Fibers

The oldest and most familiar high performance fiber is glass. Glass fibers are relatively inflexible and not suitable for many textile applications. However, they can be found in a wide range of end uses such as insulation, fire resistant fabrics and reinforcing materials for plastic composites. In recent years optical quality fiberglass has revolutionized the communication industry [5].

2.2.2.2 Carbon Fibers

An entirely different group of strong fibers from polymeric materials is formed by carbon fibers. Carbon fibers with a high strength and stiffness can be produced form polymeric materials by subjecting suitable precursor fibers to a high temperature treatment (1000 -3000°C). This removes practically all non-carbon elements and results in a fibers with a very high carbon content (>99%) which is present mainly in the form of graphite. The high strength and stiffness of these fibers can be related to the orientation of the graphite layer-planes in the fiber direction [6]. The amount of orientation achieved in carbon fibers depends mainly on two factors: the anisotropy of the precursor of fiber and the final heat treatment temperature. Linear, high molecular weight precursor materials, such as polyacrylonitrile (PAN), can be conveniently oriented by means of hot drawing. The tensile strength and Young's modulus of PAN based carbon fiber appears to be directly related to the draw ratio of precursors. However, the tendency of oriented polymer fibers to undergo shrinkage upon heating makes it necessary to apply stress during stabilization and subsequent carbonization. Similarly, cellulosic precursor fibers need to be stress-graphitized in order to obtain good mechanical properties [7]. A different type of carbon fiber is derived from so-called mesophase pitches, which consist of a mixture of aromatic hydrocarbons that exhibit liquid-crystalline properties at elevated temperatures. This liquid crystalline phase is easily orientable by shear or elongation and can be extended and drawn into highly oriented fibers. Due to their specific structure, these precursor filaments can be converted into ultra-high modulus carbon or graphite fibers without the application of stress.

The formation of carbon fibers usually involves three stages: low temperature decomposition (<400°C), carbonization (<1500°C) and graphitization (>2500°C). The carbon fibers obtained after the carbonization have lost most of their non-carbon impurities and possess a so-called turbostratic structure, in which graphite layer planes are randomly rotated with respect to each other. Further heat treatment at temperature above 2500°C does not cause any appreciable decrease in the weight of fiber, but improves the ordering and orientation of the crystallites in the direction of the fiber axis [8]. This results in better mechanical properties of the final carbon fiber. The Young's modulus of carbon fibers has been found to be related directly to the final heat-treatment temperature during graphitization [9].

2.2.3 Stiff-Chain High Performance Fibers

2.2.3.1 Aramid Fibers

Aramid fiber is based on poly (p-phenylene terephthalamide) (PPD-T) polymer. Aramid is produced by a classical poly-condensation of PPD (p-phenylene diamine) and terephthaloyl chloride (TCl) in amide solvent. Structure of aramid fiber is shown in Fig. 2.3.

The degree of molecular order of aramid in solution depends on the concentration. As the polymer concentration increase from 5 to about 12%, the solution viscosity increases as expected. The rod like molecule will take a form as in Fig. 2.4a. However, as the concentration increases further, the rod like polymer will form a nematic state with high degree of orientation (see Fig. 2.4b). As a result, the solution viscosity will drop instead of increase. When this highly anisotropic material is under shear, or elongation flow like fiber spinning process, the molecule of the extrudate will further align with the fiber axis to give the resulting fiber its orientation

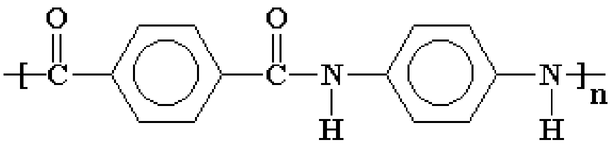


Fig. 2.3- Structure of aramid fiber

The aramid solution is spun by a process called the dry-jet spinning. In this process, an anisotropic solution of PPD-T is extruded through the air gap into a coagulated bath. The resultant yarn after coagulation is washed and dried.

(a) (b)

Fig. 2.4- Distribution of rod-like aramid structure in diluted solvent, (a) in liquid crystalline arrays, (b) nematic state for one array

Aramid fibers are used on the leading edges and undersides of wings and control surfaces of airplanes to protect against damage that might occur from rocks and other debris kicked up during takeoffs and landings. Aramids are also used for making missile launch cases where damage from handling or transport might smash-up a carbon fiber case. In some of these applications, the aramid is used only as a surface layer, with the bulk of the part being made from carbon fiber or fiberglass. Aramid fibers are also used successfully for ballistic vests, helmets and vehicles.

2.2.3.2 Poly (p-phenylenebenzobisoxazole) (PBO) Fibers

PBO is another high strength fiber based on repeating aromatic structures which is a recent addition to the market (see Fig. 2.5). PBO exhibits very good tensile strength and high modulus, which are useful in reinforcing applications. High performance properties of PBO are originated from the rod-like nature of the polymer chain which also makes the processing of fiber from polymer fairly difficult. The development of production technology on PBO fiber spinning took a long time due to the difficult nature of rod like structure. In 1991 Dow Chemical decided to work with Toyobo. Their joint development resulted in a unique spinning technology, opening the way to the industrial production of PBO fiber.

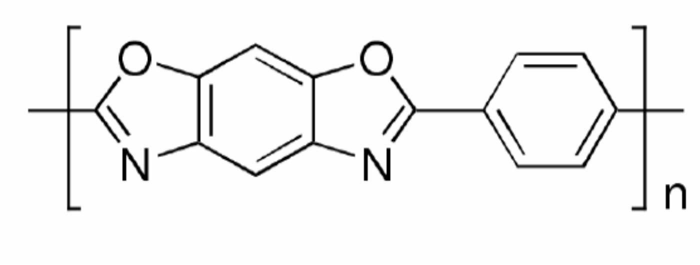


Fig. 2.5- Structure of PBO fiber

PBO is polymerized from diaminorecorcinol dihydrochloride (DAR 2HCl) and terephthalic acid (TA) in polyphosphoric acid (PPA). Current PBO fiber is spun from spinning dope with phosphoric acid solution using air-gap wet spinning technology. On a coagulation process, fiber structure formation through phase separation should occur. The first filaments extruded from a spinneret transform to a swollen micro fibrillar network when the nematic rigid-like solution touches a coagulant. Passing through the coagulation process, the network loses its open spaces and forms dense fibrillar structure. The coagulated fiber is subsequently washed and dried [5].

2.2.3.3 M-5 Fibers

M-5 fiber is a high performance fiber. M-5 fiber is based on the rigid-rod polymer poly{diimidazo pyridinylene (dihydroxy) phenylene}; the polymer repeat unit is illustrated in Fig. 2.6. The crystal structure of M-5 is different from all other high strength fibers; the fiber features typical covalent bonding in the main chain direction, but it also features a hydrogen bonded network in the lateral dimensions. M-5 fibers currently have an average modulus of 310 GPa, (i.e. substantially higher than 95% of the carbon fibers), and average tenacities currently higher than aramids (such as Kevlar or Twaron) and on a par with PBO fibers (such as Zylon), at up to 5.8 GPa [10].

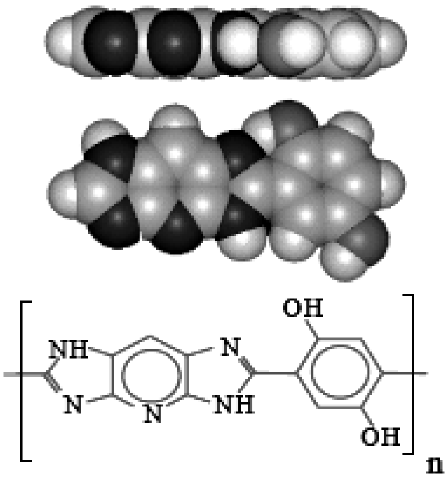


Fig. 2.6 - M-5 polymer repeat unit

2.2.4 Flexible-Chain High Performance Fibers

The production of high strength, high modulus fibers from stiff-chain polymers (aramid) at the end of 1960s and beginning of the 1970s stimulated work on the possibilities of producing high-strength and high modulus fibers from the flexible-chain polymers (polyethylene, polypropylene, PVA etc.) widely used in industry. In contrast to stiff-chain macromolecules easily oriented along the fiber axis, macromolecules of flexible-chain polymers form pleated-conformation structures. Transformation of pleated crystallites (lamellae) into structures with ultimately extended and oriented macromolecules is the main problem in obtaining high strength, high modulus fibers from flexible-chain polymers. Recently, considerable success has been achieved in this direction with formation from melt and solution of flexible-chain polymers (polyethylene in first place).

2.2.4.1 High Strength Polyethylene Fibers

The formation of polyethylene melts with given molecular mass distributions, with further thermal drawing at high ratios, has given superdrawn crystalline fibers. Through a solid phase coextrusion of mats of single polyethylene crystals, fibers with monocrystalline structure and Young’s modulus of 222 GPa have been spun. Spinning from solutions or gels of polyethylene polymer with molecular mass over 2.5 x10^5 g/mol in hydrocarbons or paraffin oil by wet method, with further multi-stage drawing of secondary gels (xerogels), spinning of polyethylene solution by the this method has made it possible to produce fibers with tensile strength of up to 5.0 GPa and modulus of elasticity of 100-200 GPa.

Although the first work on formation from gels appeared at the end of the 1950s, industrial production was only accomplished much later, in the 1980s. On an industrial scale, these fibers are produced by Allied (USA) under the trade brands Spectra-900, Spectra-1000 and Spectra-2000 and by Toyobo and Toyo Boseki (Japan). The latter together with Dyneema (Holland) produces fibers on both industrial and experimental-industrial scales.

2.2.4.2 Poly(vinylidene fluoride) Fibers

Other Flexible-Chain High Performance Fibers developed during the last few years are also of interest. From melts of high molecular weight poly(vinylidene fluoride), monofilaments can be spun at low rate that, after drawing at high ratio, have tensile strengths of 2.5-2.6 GPa, elongation at rupture of 10 % and initial Yong's modulus of 23 GPa. The fibers are characterized by a crystalline structure with an average crystalline size of 20 nm and high degree of chain orientation.

2.2.4.3 PVA Fibers

Like polyethylene, PVA fibers are spun from solutions in an inorganic solvent-water mixture, at a concentration of 2-35 %, following gel technology. After thermal drawing at 220-240°C with a general ratio of up to 30, fibers are obtained with a high degree of orientation, crystalline structure, tensile strength of 2.18-3.9 GPa and initial modulus of 54.5-79.5 GPa [11].

2.3 Polyethylene

Polyethylene is a polymer consisting of long chains of the monomer ethylene (or ethene).The ethene molecule C_2H_4 is $CH_2=CH_2$. Two CH_2 groups connected by a double bond, thus polyethylene contains the chemical elements carbon and hydrogen. Polethylene repeat unit is shown in Fig. 2.7.

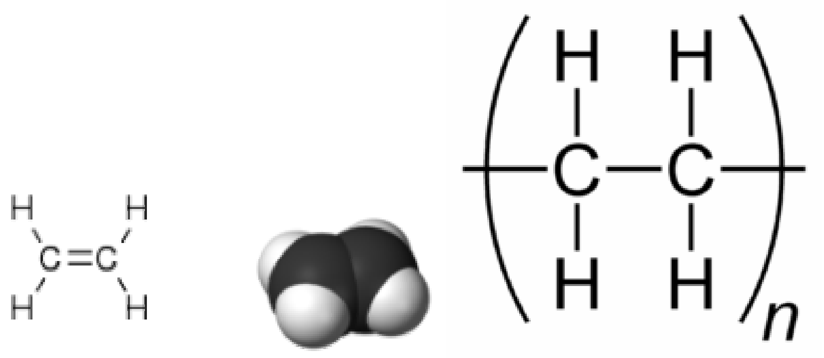


Fig. 2.7 - Polyethylene repeat unit

Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene [12].

2.3.1 Evolution of Polyethylene

Polyethylene, one of the major bulk polymers of this century, was found, more or less accidentally, at ICI company in the mid-thirties. A major break through in polymerization technology was realized in the mid fifties. Ziegler and Natta discovered heterogonous catalysts which enabled polymer scientists and engineers to produce linear polyethylene grades. Almost immediately after this important discovery, Keller [13], Till [14] found independently that linear polyethylene could crystallize from dilute solutions into thin platelet crystals, called lamellae. Since the contour length of polyethylene molecules vastly exceeds the thickness of these thin platelet crystals, typically in the range of

100 A°, Keller concluded on the basis of electron-diffraction experiments that the macromolecules are folded in the crystals, as shown schematically in Figure 2.8.

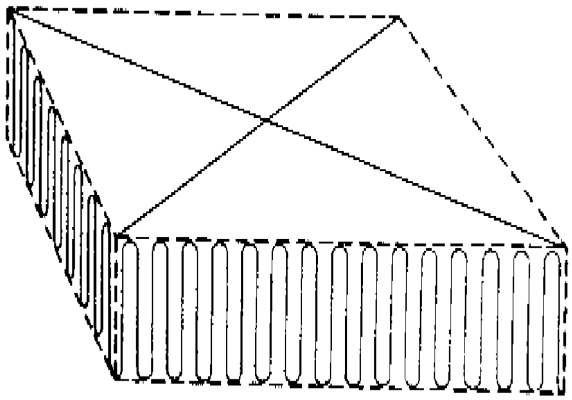


Fig. 2.8- Schematic representation of folded macromolecules within a crystal of polyethylene

Since then numerous studies have been devoted to the crystallization kinetics, morphology and structure of linear polyethylene. Polyethylene is without any doubt the most studied polymer in polymer science, due to its simple chemical structure, the availability of a large range of molecular weights, and the fast crystallization into well defined crystalline entities.

Although well defined chain-folded polyethylene crystals can be only grown from very dilute solutions, the tendency of chain-folding is present also upon crystallization from the melt. Due to this crystallization process, the mechanical properties of these linear polyethylene grades are significantly superior when compared with branched, less crystalline low density polyethylenes.

In the seventies, another important issue appeared in the polyethylene history ; orientation of polyethylene into chain-extended structures, Challenged by theoretical considerations which showed that the modulus of a single stretched (extended) polyethylene chain could amount up to 300 GPa [15], several researchers started basic studies to transform polyethylene from folded-chain crystal morphology into a more oriented/chain extended structure.

Notably, Ward et al. found that by tensile drawing of solid polyethylene, in a temperature range closed to but below the melting temperature, a pronounced increase in the modulus could be achieved in the drawing direction, typically in the range of 70-80 GPa [16]. Realize

Via a slow path, the first steps on which were taken by Pennings et al. [17] in the mid seventies with his stirred induced crystallizaion in solutions of high molecular weight polyethylene, another breakthrough took place at the end of the 1970s at DSM Research, i.e. the so called solution (gel) spinning process for ultra high molecular weight polyethylene resulting in fibers with tensile moduli above 100 Gpa and tenacities of approx. 3 GPa [18,19].

2.3.2 Classification of Polyethylene

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight [12].

- High density polyethylene (HDPE)
- Cross-linked polyethylene (PEX or XLPE)
- Medium density polyethylene (MDPE)
- Low density polyethylene (LDPE)
- Linear low density polyethylene (LLDPE)
- Very low density polyethylene (VLDPE)
- Ultra high molecular weight polyethylene (UHMWPE)

2.3.2.1 High Density Polyethylene (HDPE)

It is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. The lack of branching is ensured by an appropriate choice of catalyst (for example, chromium catalysts or Ziegler-Natta catalysts) and reaction conditions. HDPE is used in products and packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes.

2.3.2.2 Cross-linked Polyethylene (PEX or XLPE)

It is a medium to high density polyethylene containing cross-link bonds introduced into the polymer structure, changing the thermoplast into an elastomer. The high temperature properties of the polymer are improved, its flow is reduced and its chemical resistance is enhanced. PEX is used in some potable-water plumbing systems because tubes made of the material can be expanded to fit over a metal nipple and it will slowly return to its original shape, forming a permanent water-tight connection.

2.3.2.3 Medium Density Polyethylene (MDPE)

It is defined by a density range of 0.926–0.940 g/cm^3. MDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. MDPE has good shock and drop resistance properties. It also is less notch sensitive than HDPE, stress cracking resistance is better than HDPE. MDPE. It is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures.

2.3.2.4 Low Density Polyethylene (LDPE)

It is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the 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. LDPE is created by free radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap.

2.3.2.5 Linear Low Density Polyethylene (LLDPE)

It is defined by a density range of 0.915–0.925 g/cm^3. LLDPE is a substantially linear polymer with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). LLDPE has higher tensile strength than LDPE, it exhibits higher impact and puncture resistance than LDPE. Lower thickness (gauge) films can be blown, compared with LDPE, with better environmental stress cracking resistance but is not as easy to process. LLDPE is used in packaging, particularly film for bags and sheets. Lower thickness may be used compared to LDPE. Cable covering, toys, lids, buckets, containers and pipe. While other applications are available, LLDPE is used predominantly in film applications due to its toughness, flexibility and relative transparency.

2.3.2.6 Very Low Density Polyethylene (VLDPE)

It is defined by a density range of 0.880–0.915 g/cm^3. VLDPE is a substantially linear polymer with high levels of short-chain branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). VLDPE is most commonly produced using metallocene catalysts due to the greater co-monomer incorporation exhibited by these catalysts. VLDPEs are used for hose and tubing, ice and frozen food bags, food packaging and stretch wrap as well as impact modifiers when blended with other polymers.

2.4 Ultra High Molecular Weight Polyethylene

Ultra high molecular weight polyethylene (UHMWPE), also known as high-modulus polyethylene (HMPE) or high-performance polyethylene (HPPE) is a subset of the thermoplastic polyethylene. It has extremely long chains, with molecular weight in the range of 2.5×10^5 – 3.5×10^6 g/mol and density of about 0.970 g/cm^3. The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. This results in a very tough material, with the highest impact strength of any thermoplastic presently made.

It is highly resistant to corrosive chemicals, with exception of oxidizing acids. It has extremely low moisture absorption, has a very low coefficient of friction, is self-lubricating, and is highly resistant to abrasion (15 times more resistant to abrasion than carbon steel). Its coefficient of friction is significantly lower than that of nylon and acetal, and is comparable to that of Teflon, but UHMWPE has better abrasion resistance than Teflon. It is odorless, tasteless, and nontoxic.

UHMWPE is available commercially either as consolidated forms, such as sheets or rods, and as fibers. UHMWPE powder may also be directly molded into the final shape of a product. Because of its resistance to wear and impact, UHMWPE continues to find increasing industrial applications, including the automotive and bottling sectors, for example. Since the 1960s, UHMWPE has also been the material of choice for total joint arthroplasty in orthopedic and spine implants. UHMWPE fibers, commercialized in the late 1970s by the Dutch chemicals company DSM, are widely used in ballistic protection, defense applications, and increasingly in medical devices as well.

2.4.1 Structure and Properties

UHMWPE is a type of polyolefin and despite relatively weak Van der Waals bonds between its molecules, derives ample strength from the length of each individual molecule. It is made up of extremely long chains of polyethylene, which all align in the same direction. Each chain is bonded to the others with so many Van der Waals bonds that the whole can support great tensile loads.

When formed to fibers, the polymer chains can attain a parallel orientation greater than 95% and a level of crystallinity of up to 85%. In contrast, Kevlar derives its strength from strong bonding between relatively short molecules.

The weak bonding between olefin molecules allows local thermal excitations to disrupt the crystalline order of a given chain piece-by-piece, giving it much poorer heat resistance than other high-strength fibers. Its melting point is around 144°C to 152°C, and it is not advisable to use UHMWPE fibers at temperatures exceeding 80 to 100 °C for long periods of time. It becomes brittle at temperatures below -150 °C.

The simple structure of the molecule also gives rise to surface and chemical properties that are rare in high-performance polymers. For example, the polar groups in most polymers easily bond to water. Because olefins have no such groups, UHMWPE does not absorb water readily, but it also does not get wet easily, which makes bonding it to other polymers difficult. For the same reasons, skin does not interact with it strongly, making the UHMWPE fiber surface feel slippery. Since UHMWPE does not contain chemical groups (such as esters, amides or hydroxylic groups) that are susceptible to attack from aggressive agents, it is very resistant to most of chemicals, UV radiation, and micro-organisms [20].

2.5 Processes for Preparation of UHMWPE fiber

The processes of making the high performance UHMWPE fiber, based on the simplest and flexible polyethylene, is extreme spectrum of processing methods for high performance fibers. Few important methods to produce UHMWPE fibers are described below [5].

2.5.1 The "Surface-Growth" Technique

Superstrong polyethylene fibers can be produced in a one-step process which essentially consists of oriented crystallization due to stretching of entangled high-molecular weight polymer molecules by subjecting dilute solutions to Couette flow while the growing fibrous crystal is being pulled out of the system. The experimental set-up of this technique is schematically represented in Fig. 2.9, encompasses a beaker usually containing dilute supercooled solutions of polyethylene in p-xylene, a cylindrical rotor made of teflon, a take-up roll and a strain gauge to measure the tension in the growing fiber.

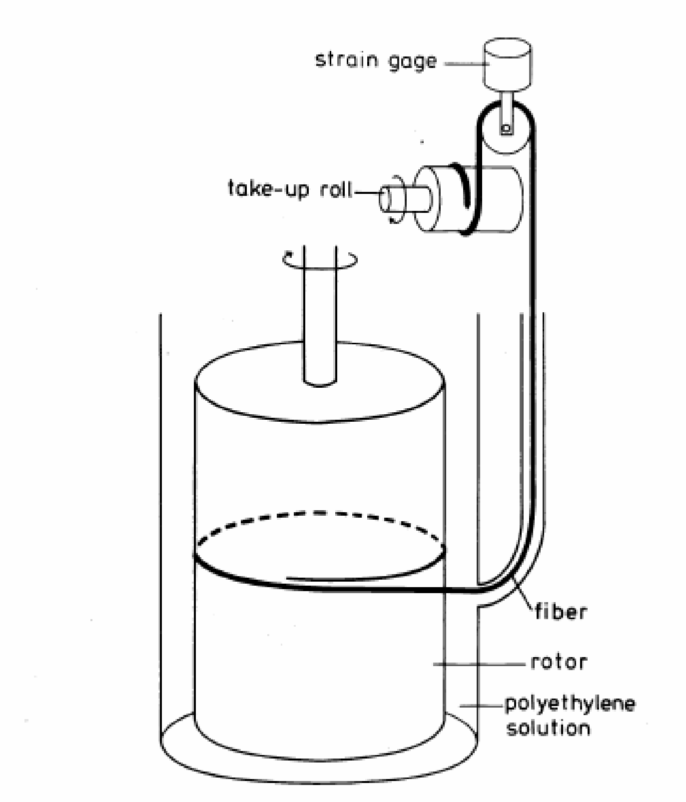


Fig. 2.9 Illustration of a Couette apparatus for surface growth of UHMWPE fiber

The general procedure of preparing these strong fibers is as follows; After dissolution of the polyethylene at 130°C the solution is cooled down to e.g.110°C in the case of p-xylene as a solvent and the rotor is set in motion.

Subsequently a fibrous seed crystal is pushed through a small pipe attached to the beaker and is submerged in the solution. It will be aligned by the flowing solution and transported towards the rotor surface by following the streamlines. Once it comes into contact with the rotor surface the seed crystal starts to grow after some induction period, thereby pulling the rope, to which the seed is connected taut. At that moment the take-up roll motor is switched on and its speed is adjusted in such a manner that it is equal to the longitudinal growth rate of the fibrous crystal. Once this steady state has been attained growth can be continued for many days [21].

According to the model for fibrous growth as shown in Fig. 2.10 it is supposed to depict that the effectiveness of the stretching of the entanglement network is actually due to two factors. First of all the gel is attached to the rotor surface by the adsorbed layer on one end and connected to the seed crystal on the other end through repetition of cilia into the network meshes. Secondly the seed crystal and rotor surface move in opposite directions. Evidently, this complex mode of oriented crystallization of entanglement networks is dependent on many variables such as take-up speed, rotor-speed, temperature, solvent quality and viscosity, polymer concentration, rotor surface roughness, etc. Several of these variables turned out to be interdependent.

A strong indication of the major effect of crystallization in this fiber formation process is the linear decrease of the fiber mass growth rate with increasing temperature. The action of the stress field on the crystallites in the fiber may be quite significant as judged from the observation that in the case the fiber breaks the portion attached to the rotor surface snaps back like a rubber band indicating that at the crystallization temperature the crystallites can disappear nearly instantaneously. Apparently lateral crystal growth, that provides the thermal stability to the crystallites, proceeds at a considerably slower pace. At relatively high crystallization temperatures the fibers become thinner while the take-up tension just increases and this frequently leads to fiber fracture.

Further, the friction between fiber and rotor surface apparently makes up a considerable part of the wind-up tension. Growth interruption could also happen as a result of the fiber being wrapped several times around the rotor. Apparently the stretching of polyethylene entanglement networks at lower temperatures is accompanied by the generation of long cilia which precipitate later on as chain-folded platelets on the fibrous backbones, whereas at higher temperatures primarily backbone material is formed. Fast crystallization in the flow direction at lower temperatures gives rise to trapping defects such as entanglements and generates disordered domains from which the cilia emerge. At higher temperatures particularly in the early stages of slow crystallization, creep is likely to occur and cilia may possibly be pulled into the stretched by filament by sliding motions through entanglement loops. Also the transport of stems through these small crystallites contributes considerably to the removal of topological constraints and the release of stress concentrations.

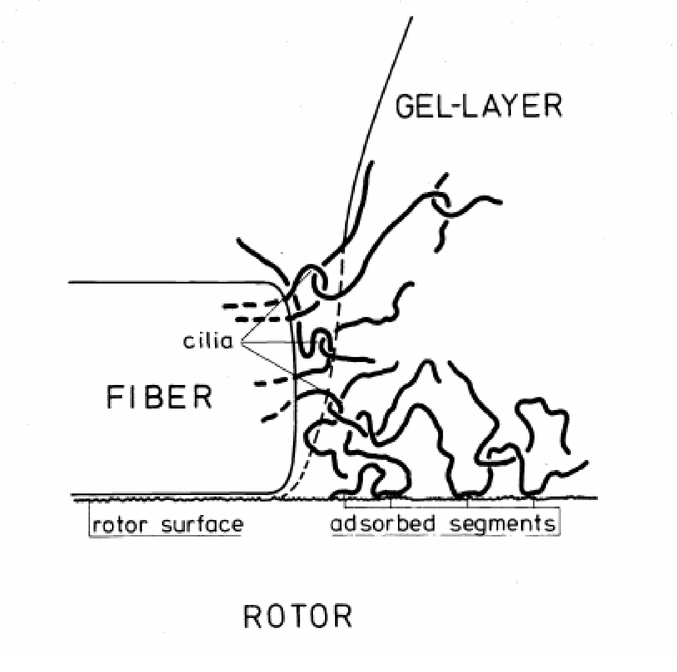


Fig. 2.10- Schematic drawing of a growing fiber in contact with molecules near the rotor surface.

One of the limitations of the 'surface-growth" technique so far encountered is that the fiber growth rate appears to be rather small. Since this limiting value is due to fiber fracture, caused for a significant part by the friction between the fiber and the rotor surface. Therefore other techniques are preferred which avoid the friction, but utilize the principle of stretching entanglement networks under controlled conditions of temperature, deformation rate, network topology and solvent quality [22].

2.5.2 High-Speed Gel -Spinning

High-speed spinning is a process in which the polymer molecules are elongated in the spinline, by applying very high winding speeds. The use of high winding speeds leads to the formation of a highly oriented and crystalline fiber in a one step procedure, in contrast to the two step procedure, in which the fibers are wound at low speeds and need to be hot drawn subsequently. Although the mechanical properties of the high-speed spun fibers are somewhat lower than the properties of the fibers that are produced in two step procedure, high-speed spinning is very advantageous process, because it combines a simple process to a very high productivity and low cost.

In high speed spinning process, the solution is made by adding the UHMWPE powder at concentration of 1-5 % to the paraffin oil at 120°C under a nitrogen atmosphere while stirring, and subsequently raising the temperature. The solution is heated to 150°C and remained at that temperature for 48 hours for the purpose of homogenizations. Upon cooling a gel is formed, which is fed to spinning apparatus, which is of the piston and cylinder type. A schematic representation of this apparatus is shown in Fig. 2.11. The piston is mechanically driven at constant speed. The hot solution is extruded into cylindrical spinline oven, which prevents rapid cooling and crystallization of the solution. The filament is wound on a rather large diameter (50 cm) winder that combines high circumferential velocities to low rotation frequencies, with the purpose of keeping the centrifugal forces relatively low. The maximum obtainable winding speed is 6000 m/min. When a bundle of filaments is cut loose from the winder most of the paraffin oil, which was squeezed out during stretching of the spinline, remained on the winder. The rest of the oil is extracted from the bundle with n-hexane [23].

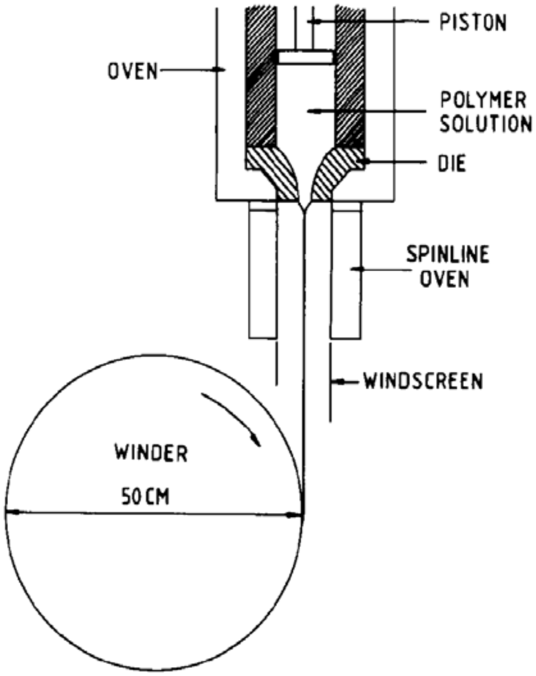


Fig. 2.11- A schematic representation of the high-speed gel spinning set up for UHMWPE solutions

One of the limitations of high speed gel spinning is that the spinline fracture may occur as a consequence or the properties of the material, when it is exposed to rapid deformation during high speed spinning. This can lead to anomalous effects like adsorption of the polymer to the die [24], pressure fluctuations in the die [25], flow induced molecular scission [26], capillary failure, melt fracture, die blockage, extrudate swell and cohesive failure [27]. A schematic explanation of extrudate behavior in terms of spinning speed is shown in Fig. 2.12 [28].

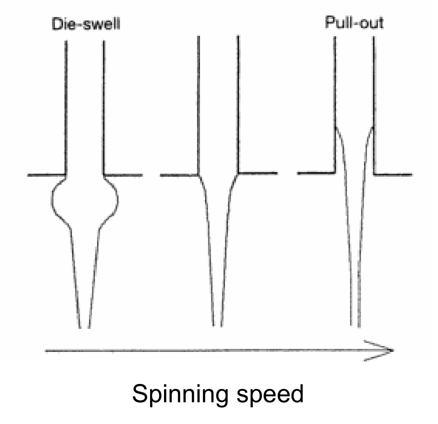


Fig. 2.12- Schematic explanation of extrudate behaviour in terms of spinning speed

2.5.3 Gel-Spinning and Hot Drawing

2.5.3.1 History of Spinning of Polyethylene

Gel-spinning of high molecular weight polyethylene goes back to investigations by Zwick who described this method and variants such as phase separation spinning in 1967. The term gel-spinning actually refers to the fact that polymer concentrations of 30 to 50 % are used and that the solvent in this case better be regarded as a plasticizer. Obviously there are quite a number of routes for transforming these gels into a filament. For instance Frenkel and Baranov et al. (described how moderately concentrated polymer solutions can be converted into fibers simply by pulling a thread from the solution meniscus and wind it up on a drum. Several aspects of the self-hardening of polymer solutions in elongational flow-fields have been described by Ziabicki. In addition to the filament formation from the dissolved state of the polymer there are also processes in which the fiber is produced from partially crystalline gels [22].

In wet spinning process fibers were spun from xylene solutions of high molecular weight polyethylene and stretched the partially crystalline gels over a hot-plate thereby making a very strong fiber with a good knot-strength. Porous fibers of high molecular weight polyethylene were manufactured by spinning xylene solutions into flowing silicone oil at 95°C. Silicone oil is a non-solvent for polyethylene and is miscible with xylene. This wet spinning process produced porous fibers which turned out to be highly deformable

In this context it is pertinent to mention the dry-spinning process known as flash-spinning as developed by White and Blades in 1963 [29]. They dissolved some 15 wt. % linear polyethylene in either methylenechloride or cyclohexane at temperatures in the range of 200 - 220°C and pressures of about 100 atmospheres. The viscosity of these superheated solutions is rather low and they can be spun with very high speeds (9000 m/min.) through orifices of 1 mm in diameter. The porosity and fibrillation due to expansion of the superheated solvent may be regulated by adding filler nucleating agents. Hot-drawing of these porous structures results in fibers and films known by the trade name Tyvek and finds application in e.g. very light air-mail envelopes [30].

2.5.3.2 Gel-Spinning

The key to achieve high strength, high modulus properties of UHMWPE is by the gel spinning process. In this process, the long, flexible and entangled molecules are dissolved in solvent like paraffin oil at 150°C for 48 hours. Mild stirring is applied as long as the powder particles are visible. In the solution molecules become disentangled and form a loosely connected network like gel. The schematic for deformation stages of UHMWPE gel with solvent is shown in Fig. 2.13. The gel, after being cooled down to room temperature, is fed into an extruder equipped with a long conical die. This extremely long die with very small entrance angle has been selected in order to minimize the severity of extrudate distortion due to melt fracture [31].

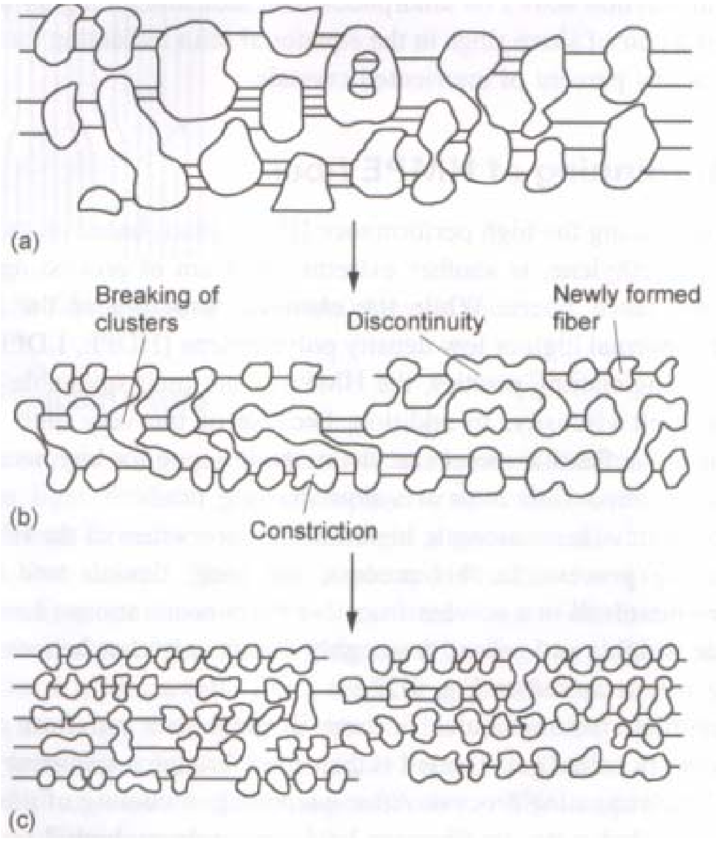


Fig. 2.13- Deformation stages of UHMWPE gel fiber with solvent

2.5.3.3 Hot Drawing

Hot drawing is well known procedure to improve the mechanical properties of polymers. In this procedure, the molecules are elongated and become oriented in the drawing direction, which increases the density of load bearing elements in the sample in that direction [32-34].

The gel spun fiber is quenched or cooled to form the loosely entangled molecule fiber. Solvent is extracted by low boiling point solvent n-hexane and porous fiber can be drawn at very high draw ratio to a highly oriented long chain crystalline high modulus fiber. The drawing is performed in hot tube at a temperature just below the melting temperature of UHMWPE. A schematic sequence to produce UHMWPE fiber by gel spinning and hot drawing is shown in Fig. 2.14 [5].

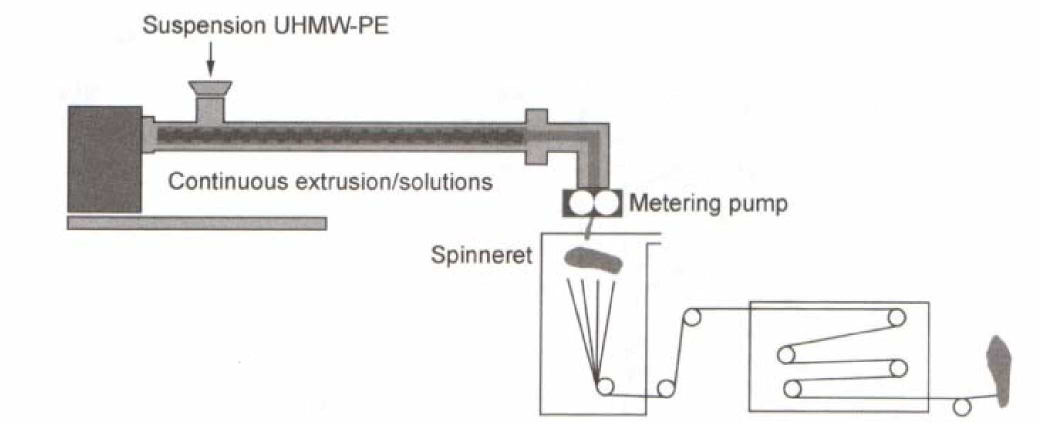


Fig. 2.14- Schematic for gel-spinning/hot-drawing of UHMWPE fiber

2.6 Factors affecting the Properties of Gel-Spun/Hot Drawn UHMWPE Fiber

The properties of the gel-spun and hot drawn UHMWPE fiber strongly depend on the polymer concentration, molecular weight, solvent quality, temperature, extrusion rate, die-shape and as-spun fiber diameter. Few of them are described below.

2.6.1 Influence of Molecular Weight

It is obvious that a certain amount of high molecular weight material is required, in order to obtain high draw ratios, and consequently exceptional mechanical properties. These molecules probably provide the coherence between the lamellar crystals (formation of tie chains) or bridge small cracks. The low molecular weight material was found to segregate between the crystals [15].

At given draw ratio, the tensile properties are highest when a polymer with a high molecular weight or narrow molecular weight distribution is used [36]. This seems to be connected to the drawing stress. Since high molecular weight polymers have high elongational melt viscosities, the stress during the drawing is also very high, which will enhance the molecular elongation and improve the orientation and the mechanical properties of the fibers. When at high draw ratios the draw stress becomes extremely high, however cohesive fracture might occur [15].

Since the tensile strength of the fibers is correlated to the number of tie molecules that bear the load, it is important that under given drawing conditions, few molecules slip through their entanglement junctions. This seems to be the case in polymer with narrow molecular weight distribution, and a high molecular weight [37].

2.6.2 Effect of Polymer Concentration

It is well known that one of the requirements for a solution to be spinnable is that the concentration of polymer in the solution has to surpass a critical concentration. This critical concentration is a decreasing function of the polymer's molecular weight, which has to be larger than the critical molecular weight for coil overlap. Both these requirements were explained by assuming that the polymer coils in solution have to be entangled in order to make the solution coherent enough to be spinnable. In the case of UHMWPE this concentration was determined by Matsuo et al. who found it to be 0.4 wt % in viscosimetry experiments [38], while Smith et al. found in film casting experiments a critical concentration of 0.07 wt % [39]. Below the critical overlap concentration fiber spinning is not possible.

Increasing the polymer concentration raises the viscoelasticity of the solution. The number of entanglements increases, and the average strand length between entanglements decreases. A flowing solution of entangled molecules obtains orientation at lower flow rates, when the polymer concentration in the solution is increased. Peiffer et al. found that the amount of orientation in the solution increases with concentration, but that the maximum orientation per chain is reduced because entanglements prevent the molecules from becoming completely stretched [40].

2.6.3 Influence of Extrusion Rate

Apart from the influence of polymer concentration, molecular weight, solvent quality, temperature and die-shape on the gel-spinning one should expect to find a strong dependence of the properties of the as-spun fiber on the extrusion rate. In particular in the case of high molecular weight polymers flow instabilities such as die-swell, elastic turbulence and spiral flow are bound to be encountered even at very small extrusion rates. It seems to be well accepted that the onset of elastic turbulence is related to a critical shear stress at the wall of the die (which is inversely proportional to the molecular weight of the polymer). It is also clear that these elastic turbulence phenomena, which inevitably lower the strength of the fiber, only occur in the case of an effective entanglement network.

These flow disturbances may be suppressed by using a conical die to reduce the elongational flow gradient at the die entrance and by pulling the extrudate immediately after leaving the die [22].

2.6.4 Effect of Drawing Temperature

The maximum draw ratio and maximum obtainable tensile properties were found to depend on the drawing temperature and rate. The optimum drawing temperature at which the molecular mobility is high enough to elongate the molecules and low enough to prevent relaxation, seems to be several degrees below the melting temperature of the polymer [41].

2.7 Deformation Behavior of Oriented Fiber

In case of oriented polyethylene structures, only weak Van der Waals interactions are operative between the oriented/extended macromolecules. The absence of stronger interactions, like hydrogen bonding is an advantage on one hand since the folded-chain crystals are easily deformed (slip) and transformed into chain-extended structures, provided that the motion of chains is not restricted by topological constraints. On the other hand, one has to pay a penalty for the ease of drawability; the oriented structure is inherently unstable with respect to static loadings since no lock-in mechanism is operative after the actual drawing process. In fact, there is no basic difference between the actual drawing process and loading the fiber in a creep experiment, although on a different time/temperature scale [42].

The deformation behavior of UHMWPE fiber can be regarded to originate from a reversible linear viscoelastic contribution and a non-linear, plastic flow contribution to the deformation acting simultaneously. Fig. 2.15 shows the schematic representation.

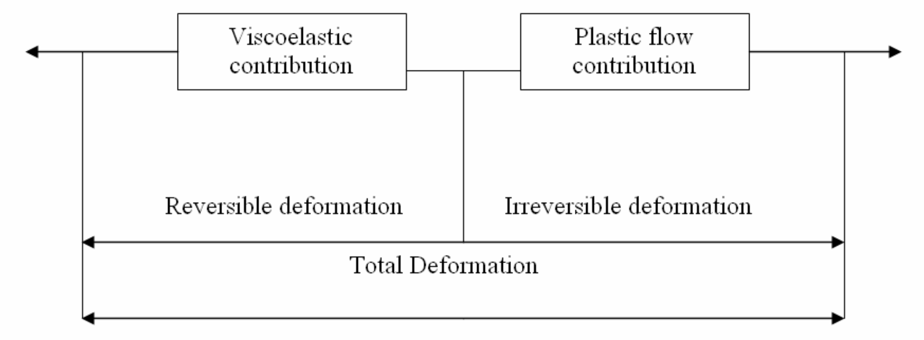


Fig. 2.15- Schematic representation of the phenomenological approach to the deformation behaviour of UHMWPE fiber

At short loading times, low stress levels or low temperature, the viscoelastic contribution dominates the deformation behaviour, the plastic flow contribution being negligible. At longer loading times, high stresses and/or temperatures, the viscoelastic contribution decreases and a constant strain rate flow contribution accounts for the irrecoverable deformation of the fiber and it will therefore be referred to as the plastic flow contribution to the deformation [43].

2.8 Mechanical Strength of High Performance Fibers

In Table 2.1, the mechanical properties of selected number of experimental as well as commercially available polymeric fibers are listed. These data illustrates the mechanical properties that can be realized in polymeric fibers, using different starting materials and fiber processes.

Table 2.1- Mechanical properties of selected polymeric fibers

Material	**Fiber-Trade name**	**Strength (GPa)**	**Modulus (GPa)**	**Strain at break (%)**	**Density (g/cm^3)**
UHMWPE	Spectra 1000	3.0	172	3.5	0.97
Aramid	Kevlar 49	2.76	124	2.5	1.44
Carbon Fiber	Thomel P100	2.25	690	0.4	2.10

The Young's modulus of a fiber is a manifestation of the way in which it responds to infinitesimal strains and consequently the modulus can be related to the unreformed fiber structure in a relatively straight forward manner. In oriented, semi-crystalline polymer fibers, the Young's modulus can be conveniently described using the Takayangi approach, in which the fiber is thought to be composed of various phases, each corresponding to a different modulus of elasticity. The overall modulus of elasticity of this composite structure can be derived from the relative amounts of the components and from the kind of mechanical coupling that exists between them. In the case of carbon fibers, the main structural parameter with respect to the Young's modulus is the orientation distribution of the graphitic basal planes [44, 45]

As can be seen in table 2.1, the modulus of elasticity that can be achieved in both carbon and polyethylene fibers are close to the theoretical limit, reflecting the high degree of orientation and structural perfection that can be achieved under the appropriate processing conditions. At the same time, the strength of these fibers is comparatively low. This effect is most pronounced in high modulus carbon fibers, which exhibit strength to modulus ratios of about 0.003. In ultra-drawn polyethylene fibers, this ratio is about 0.025. For both materials, a value of 0.1 is predicted theoretically. This observation is usually interpreted in terms of structural flaws, which depress the strength but do not significantly affect the Young's modulus of the material. According to Griffith, a crack length of '**c**' in a linear elastic material with Young's modulus '**E**' and surface tension '**γ**' can propagate under a stress '**α**' , that is given by the following relation:

$$\sigma = \left(\frac{2\,E\,\gamma}{\pi\,c}\right)^{1/2} \qquad \text{------------ (2.1)}$$

This relationship demonstrates that the presence of large defects will lead to a considerable reduction of the strength of the material. However, its applicability to strong polymeric fibers is still a matter of debate. In high modulus carbon fibers as well as in high strength polyethylene fibers, the fracture surfaces do not normally show any recognizable initiating defects. Furthermore, a fractographic study showed that oriented polymers are completely notch-insensitive, indicating, that the critical flaw criterion does not hold.

A number of alternative fracture mechanisms have been proposed in order to obtain a more realistic description of failure in strong fibers. For carbon fibers, fracture initiation has been interpreted in terms of stress concentration arising from dislocation pile up at crystallite boundaries [46]. Rynolds and Sharp proposed the so called crystallite shear limit for carbon fiber fracture, which is based on the idea that the graphitic crystallites are weakest in the shear on the basal planes. According to this mechanism, fracture is initiated at large, highly misoriented crystallites.

In high modulus fibers from linear thermoplastic polymers, such as polyethylene, the comparatively low strengths appear to be related to incomplete crystallization, rather than incomplete orientation as in the case of carbon fibers. During drawing of gelation-crystallized polyethylene fibers, the crystallites reach the maximum orientation already at low draw ratios, whereas the crystallinity in these fibers particularly never exceeds 90 %, even at very high draw ratios. Further crystallization is hampered by topological defects, like entanglements, which can be removed by drawing and which give rise to defect regions. The fracture mechanism of these fibers is usually explained in terms of primary bond rupture at these sites. A detailed study of the fracture behavior of high strength polyethylene fibers, however showed that apart from chain scissioning, the breakage of secondary bonds also plays an important role. It has been suggested that stress induced transitions, including solid-solid phase transitions and melting may also be involved in the fracture process of highly ordered fibers [47].

2.9 Microfibrillar Model for Fiber structure

2.9.1 Morphology

By hot drawing of gel spun ultra high molecular weight polyethylene (UHMWPE) fibers, the loosely connected lamellar structure of these fibers is gradually transformed into fibrillar morphology with excellent mechanical properties. This transformation proceeds through micronecking of lamellae of the original unoriented material, where so called tie molecules are formed by the unfolding of chains when lamellae are disrupted at the micronecks [12].

Beyond the point of complete unfolding of the lamellae, further extension proceeds by slippage of molecular chains through entanglement hooks. The basic element of the fibrillar structure formed in this way is the microfibril that is thought to consist of an almost infinite sequence of crystalline blocks, interrupted by disordered domains, in which imperfections like chain entanglements are collected. According to Peterlin, the high axial modulus and strength of the microfibril arises from the presence of "Taut Tie Molecules" (TTM) in the disordered domains that form the connection between adjacent crystalline blocks (see Fig. 2.16).

One usually discerns intra-fibrillar tie molecules, connecting adjacent crystalline blocks within one microfibril, and inter-fibrillar tie molecules, that form a lateral connection between individual microfibrils. In drawn polyethylene, the number of inter-fibrillar tie molecules is much smaller than the number of intra-fibrillar tie molecules. Since the disordered domains are defect zones, where the cross-sectional area of the microfibril is only partially occupied by load carrying chains, fracture is likely to be initiated there [48,49].

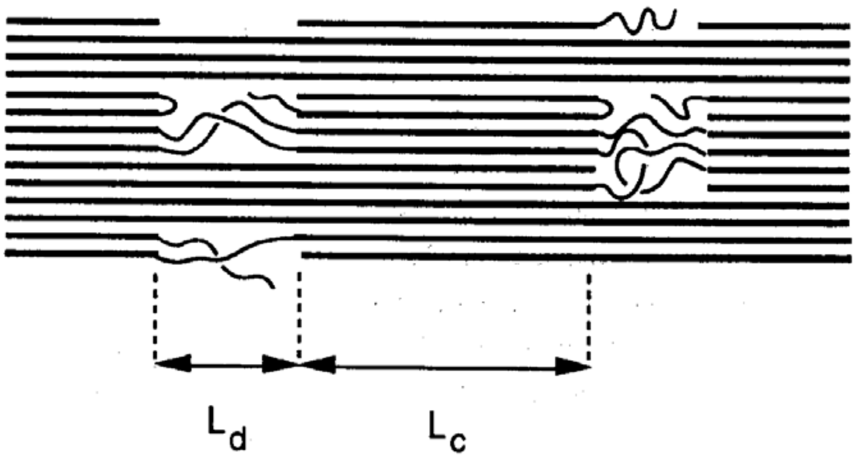


Fig. 2.16- Schematic representation of the elementary microfibril, showing crystalline blocks with length Lc and disordered domains with length Ld

2.9.2 Micromechanical Modeling

At very small stresses the response of the axially strained fiber is described by the Young's modulus. The fibrous structure can be regarded as a multi phase system, where the various phases correspond to "Extended Chain Crystals" (ECC), "Taut Tie Molecules" (TTM) and amorphous material.

Polymer chains in extended confirmation, i.e. ECC and TTM, are characterized by the crystal modulus of the polymer Ec, whereas the amorphous material is characterized by Ea.

The overall Young's modulus of the composite structure depends on the relative amounts of ECC, TTM and amorphous material, and on the way in which they are mechanically coupled. Basically two different types of mechanical coupling can be discerned. First of all, the disordered domains can be thought of as an amorphous phase that is reinforced with TTM. The reinforced amorphous layer acts in series with crystalline block. This arrangement is shown in Fig. 2.17a and is termed uniform-stress model. Although this terminology is somewhat misleading, it means that the alternate crystalline blocks and disordered domains are subjected to the same macroscopic stress. As the TTM spanning the disordered domains occupy only a fraction of the microfibril, the individual tie molecules experience a stress that is much higher than the bulk stress, and therefore the uniform stress model does not imply a uniform stress distribution on molecular level. The uniform-stress model represents the situation where TTM, or small aggregates of TTM are dispersed over the width of the microfibril. In the case of an extreme bundling of TTM in the disordered domains, the TTM can be thought of as a continuous 'fiber fraction' that acts in parallel with the alternating crystalline and amorphous layers Fig. 2.18b. As a result of this parallel coupling, TTM and alternating crystalline and amorphous layers experience the same strain and this arrangement is therefore termed 'uniform strain model' [50].

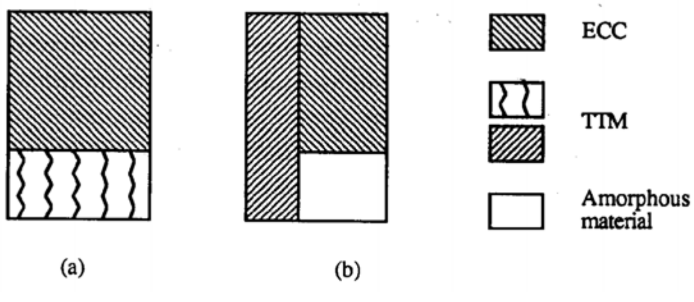


Fig. 2.17- Schematic representation of the fiber structure with ECC, TTM and amorphous material (a) uniform stress model and (b) uniform strain model

2.10 References

1. R.J. Young, P.A. Lovell, “Introduction to polymers”, Chapman and Hall, 2nd ed., 1-3, (1991)
2. P.J. Lemstra, Bussink, VNCI magazine, **24**, 10-15, (1989).
3. W.F. Smith, “Principles of Materials Science and Engineering”, McGraw-Hill Publishing Co., 2nd ed., 321-322, (1990).
4. http://en.wikipedia.org/wiki/ Fiber
5. A. Bhatnagar, “Lightweight Ballistic Composites”, Woodhaed Puublishing Lim., 189-208, (2006).
6. G.A. Cooper and R.M. Mayer, *J.Mater. Sci.*, **6**, 60, (1971).
7. J.B. Donnet, R.C. Bansal, “Carbon Fibers”, Marcel Dekker Inc., 2nd ed., (1990).
8. M.K. Jain, A.S. Abhiraman, *J.Mater. Sci.*, **22**, 278, (1987).
9. J.W. Johnson, Appl. Pol. Symp., **9**, 229, (1969).
10. J. C. L. Hageman, J. W. van der Horst, R.A. De Groot, Polymer, **40**, 1313, (1999)
11. V.I. Kostikov, “Fiber Science and Technology”, Chapman and Hall, 1st ed., 387-391, (1995).
12. http://en.wikipedia.org/wiki/Polyethylene
13. A. Keller, Phil. Mag., **2**, 1171, (1957).
14. P.H. Till, J. Polym. Sci., **24**, 301, (1957).
15. K. Tashiro, M. Kobayashi, H. Tadokoro, Macromol., **11**, 914, (1978).
16. G. Capaccio, I.M. Ward, Polymer, **15**, 233 (1974).
17. A. Zwijnenburg, A.J. Pennings, Coll. Polym. Sci., **254**, 868, (1976).
18. P.Smith, P.J. Lemstra, US Patent, 4344908, 4422993, 4430383, 4436689.
19. P.J. Lemstra, 13th Discussion Conference, Inst. Macromol. Chem. Czech. Ac. Sci., Prague, July, 1990.
20. http://www.google.com.pk/search?hl=en&q=UHMWPE
21. J.C.M. Torfs, A.J. Pennings, J. Appl. Polym.Sci., **26**, 303, (1980).
22. A.J. Pennings, J. Smook, J. de Boer, S. Gogolewski, P.F. van Hutten. Pure & Appi. Chem., **55**, 777-798, (1983).
23. A. Ziabicki, H. Kawai, “High Speed Fiber Spinning”, John Willey, (1985).
24. J. Smoke, A.J. Pennings, *J.Mater. Sci.*, **19**, 31, (1984).
25. R.W. Myerholtz, J. Appl. Polym. Sci., **11**, 687 (1967).
26. J.A. Odell, A.J. Muller, K.A. Narh, A.Keller, Macromol, **23**, 3092, (1990).
27. T.Nakajima, K. Kajiwara, J. E. McIntyre, “Advanced Fiber Spinning Technology”, Woodhead Publishing Lim.,174-184, (1994).
28. A.Ziabcki, "Fundamentals of Fiber Formation”, John Willey, (1976).
29. H. Blades, J.R. White, US Patent 3081519.
30. R.G. Parrish, US Patent 3277221.
31. J.P. Tordella, J. Appl. Phy., 27, 454.
32. P. Smith, P.J. Lemstra, *J.Mater. Sci.*, **15**, 505-514, (1980).
33. I.M. Ward, “*Developments in Oriented Polymers-2*”, Applied Science, 39-77, (1970).
34. J.P. Penning, D.J. Dijkstra, A.J. Pennings, *J. Mater. Sci.,* **26**, 4721-4730, (1991).
35. S.B. Warner, J. Polym. Sci., Phys ed., **16**, 2139, (1978).

36. W. Wu, W.B. Black, Polym. Eng. Sci., **19**, 1163, (1969).
37. J.P. Pennings, H.V.D. Werff, M. Roukema, A.J. Pennings, Polym. Bull., **23**, 347, (1990)
38. C. Swaatari, T. Okumura, M. Matsuo, Polymer, **18**, 741, (1986).
39. P. Smith, P.J. Lemstra, H.C.Booy, J. Polym. Sci., Phys ed., **19**, 877, (1981).
40. D.G. Peiffer, M.W. Kim, R.D. Lundberg, Polymer, **27**, 493, (1986).
41. Y. Termonia, S.R. Allen, P. Smith, Macromol, **21**, 3485, (1988).
42. A. Ciferri, I.M. Ward, " Ultra-High Modulus Polymers", Appl. Sci. Publ., (1979).
43. M.A. Wilding, I.M. Ward, Polymer, **22**, 870-876, (1981).
44. W. Ruland, App. Polym. Symp., **9**, 293, (1969).
45. J. Smoke, G.J.H. Vos, H.L. Doppert, App. Polym. Sci., **41**, 105, (1990).
46. S.N. Zhurkov, Int. J. Fract. Mech., **1**, 311, (1965).
47. D.C. Prevorsek, J. Polym. Sci. Symp., **32**, 343, (1971).
48. J. Smoke, A.J. Pennings, *Coll. Polym. Sci.*, **262**, 712, (1984).
49. A. Peterlin, *Coll. Polym. Sci.*, **265**, 357, (1987).
50. B. Fanconi, J.R. Robalt, J. Polym. Sci., Phys ed., **23**, 1201, (1985).

CHAPTER 3

EXPERIMENTAL TECHNIQUES AND PROCEDURES

3.1 Materials

The preparatory material used in this experimental work was a solution or gel of 7% by weight UHMWPE powder in paraffin oil. The UHMWPE was locally synthesized, having molecular weight in the range of 1.0 -1.5 x10^6 g/mol. This gel was used to conduct the gel spinning and hot drawing processes because due to the high melt viscosity, UHMWPEF is not melt spinnable [1].

3.2 Processing Equipments

3.2.1 Extruder

Single-screw extruders are industrial devices used in the production of rubbers, foams and polymers, and in the mixing of foodstuffs. In a conventional extruder apparatus such as that shown in Fig. 3.1, solid material is fed through a hopper onto a rotating screw mounted along the axis of a long barrel. The solid material enters the melting section where it is heated, melted, and passed through into the metering zone. Here the melt is mixed prior to being ejected through the die to form the final product [2].

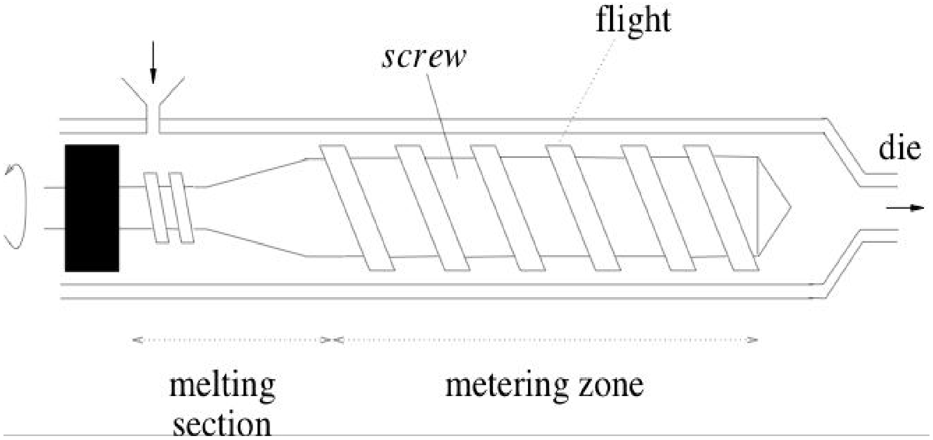


Fig. 3.1- Schematic representation of a single screw extruder

Extruder (of local make) used for forming gel-fiber of UHMWPE in this study, having the screw diameter of 30 mm and length of 600 mm (L/D ratio = 20). The drive power was 3 H.P. The heating elements employed were 1000 W. The extruder was equipped with conical single hole die of 40 mm length 28 mm inlet diameter and 3mm exit diameter for first experiment. For second experiment, die exit diameter was 1.4 mm keeping all the other dimensions same.

3.2.2 Hot Drawing Set-up

A set-up for hot drawing was designed and fabricated to carry out this experimental work. Fig. 3.2 shows the schematic diagram of fiber stretching in that particular apparatus.

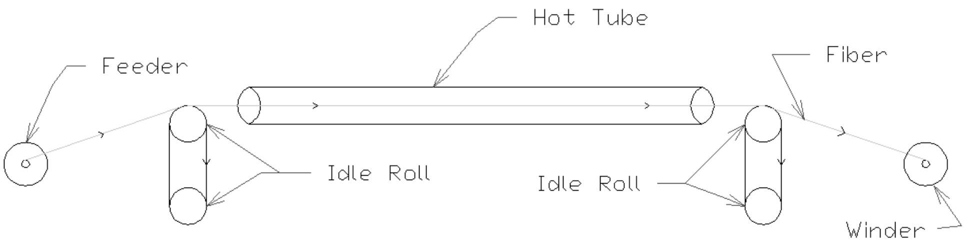


Fig. 3.2- Schematic diagram of the hot drawing set-up

The set-up for hot drawing consisted of a stainless steel pipe of 1500 mm (= 1.5 m) length, 50 mm outer diameter and 40 mm inner diameter. A heating element of 1000 W (Iso-pad) was wounded onto this pipe to provide the necessary heating inside. To prevent the heat losses to atmosphere, hot tube was wrapped with ceramic wool. To sense the inside temperature of the tube, a K-type thermocouple was fixed in the hole provided at middle of hot tube. A digital temperature controller was connected with heater and thermocouple to maintain the required temperature for hot drawing process. On each end of the hot tube, two free moving pullies of aluminum having the diameter of 50 mm and thickness of 25 mm were aligned. Two motors (1.5 H.P.) were attuned on both sides of the tube to perform as fiber's feeder and winder. To precisely control the fiber feed-up and take-up velocities during hot drawing mechanism, these motors were attached with digital speed converters. The process line diagram for hot drawing of UHMWPE fiber is shown in Fig. 3.3.

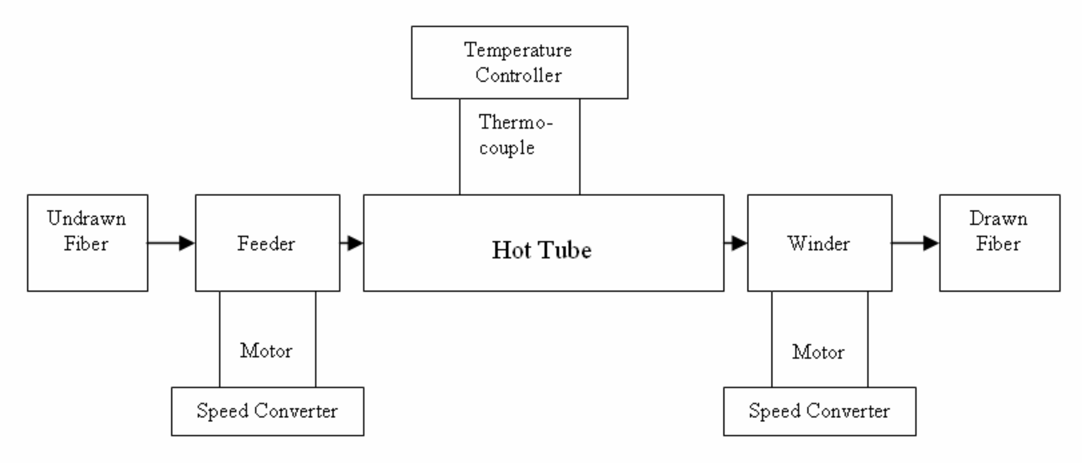


Fig. 3.3- Process - line diagram for hot drawing

3.3 Processing Detail

Following is the flow chart of the procedure for making ultra high strength polyethylene fiber:

Gel of 7% by weight of UHMWPE in paraffin oil
▼
Extrusion at 190ºC
▼
Gel Spun fiber
▼
Extraction with n-Hexane
▼
Porous Fiber
▼
Hot drawing at 110ºC
▼
Ultra high strength Polyethylene Fiber

3.3.1 Gel- Spinning

An extruder comprise of various functional zones to extrude the plastic materials [3]. In this experimental work, the extruder was operated at 5 rpm and 190ºC. The UHMWPE-gel was cut into small pieces and fed into hopper of the extruder. From hopper, the gel came to solid conveying zone, from where it was conveyed to the melting zone. Melting took place in melting zone and then from melt conveying zone the gel is forced through the die. The deformation and compression of gel by the extruder screw caused exudation of paraffin oil from the gel. This liquid backed up in the extruder barrel and was discharged from the hopper end of the extruder. At the exit end of the extruder, hot gel fibers of 3mm and 1.4 mm were produced for experiment -1 and experiment-2 respectively depending on the exit diameter of the die. The said hot gel fiber was cooled in water adjacent to the exit end of extruder and collected with the help of winder.

3.3.2 Solvent -Extraction

The non-volatile paraffin oil solvent was extracted from the extruded gel fiber using low boiling point solvent like n- hexane for 48 hours at constant length. The extracted gel fiber was dried under vacuum at 50ºC for 15 minutes. Thus a porous gel fiber of UHMWPE was obtained.

3.3.3 Hot Drawing

The drawing of porous gel fiber of UHMWPE was carried out with the help of hot drawing set-up (shown in Fig. 3.2). Hot drawing is conducted at several degrees below the melting temperature of UHMPWPE (137ºC) [4,5]. Therefore, the temperature of hot tube was maintained at 110ºC during the experiments. To adjust the speed of fiber's feeder and winder, the residence time of fiber is determined as below.

Thermal Transport: Calculation of Residence Time

The time necessary to heat the fiber's centre to 110ºC (383 K) was calculated with the following equation [6, 7]:

$$T = T_O + \Delta T \left(1 - e^{-\frac{\pi^2 a\, t}{d^2}} \right) \qquad \text{------------------------ (3.1)}$$

Where;

T = Temperature of the fiber's centre

T_o = Room Temperature = 298 K

ΔT = Temperature difference between oven and fiber = 383 K – 298 K = 85 K

a = Thermal diffusion coefficient = $\lambda / \rho c$

λ = Heat conductivity = 0.1 W / m.K

ρ = Density = 970 kg/m^3

a = 5.425×10^{-8} m^2/sec

c = Heat Capacity = 1900 J / kg.K

d = Distance of heat transport = radius of the fiber

t = Time required to heat the fiber's centre

By means of the eq. 3.1 and above data, residence time for gel fiber of 3 mm and 1.4 mm diameters were determined as 17 seconds and 4 seconds respectively.

Depending on the residence time, the fiber's feeder and winder speeds were adjusted at 0.5 rpm and 2.5 rpm respectively for 3mm gel fiber, whereas for 1.4 mm gel fiber the speeds of feeder and winder were tuned at 1.5 rpm and 3.5 rpm respectively. To achieve high draw ratio fibers are stretched repeatedly.

3.4 Testing and Characterization

3.4.1 Tensile Testing

Tensile tests were carried out on hot drawn UHMWPE fibers using the Hounsfield – H10KS tensile testing equipment, at crosshead speed of

12mm/min and a sample gauge lengths of 25 mm at room temperature [8, 9]. The ultimate tensile strength was calculated by dividing the ultimate force by the initial cross-sectional area of the fiber, which was calculated from its length and weight, taking density of 0.970 g/cm^3. Modulus was determined by following the Hook's law i.e., by dividing the stress by strain in elastic range of stress – strain plot.

3.4.2 Morphology Study

The surface morphology of the fibers drawn from different diameter gel fibers and at various draw ratios was characterized by Scanning Electron Microscope (SEM) at 20 kV. The sample fibers were covered with a thin gold layer to ensure sufficient electrical conductivity.

3.4.3 Thermal Analysis

Thermal properties of hot drawn fiber specimens were performed on a SETARAM- DSC131 Differential Scanning Calorimeter. All scans were carried out at a heating rate of 8 ºC /min over a temperature range from 25 to 200 ºC in nitrogen atmosphere [8]. Samples weighing about 3.6 mg were placed in the standard aluminum sample pans for determination of their thermal properties.

3.5 Testing and Characterizing Tools

3.5.1 Universal Testing Machine (UTM)

Tensile test is used to evaluate the strength and other mechanical properties of metals, alloys and polymers etc. In this test the sample material is pulled to failure at constant rate. Fig. 3.3 is picture of a modern tensile testing machine [3].

There are many types of testing machines. The most common are universal testing machines (UTM), which test materials in tension, compression or bending. The primary use of the testing machine is to create the stress-strain diagram. Once the diagram is generated, a pencil and straight edge or computer algorithm can be used to calculate yield strength, Young's Modulus, tensile strength or percent elongation.

There are two classes of testing machines, electromechanical and hydraulic. The electromechanical machine uses an electric motor, gear reduction system and one, two or four screws to move the crosshead up or down. A range of crosshead speeds can be achieved by changing the speed of the motor. A microprocessor based closed-loop servo system can be implemented to accurately control the speed of the crosshead.

Fig. 3.4-Tensile testing machine

A hydraulic testing machine uses either a single or dual acting piston to move the crosshead up or down. In a manually operated machine, the operator adjusts a needle valve to control the rate of loading. In a closed-loop hydraulic system, the needle valve is replaced by an electrically operated servo-valve for precise control.

In general, the electromechanical machine is capable of a wide range of test speeds and long crosshead displacements, whereas the hydraulic machine is a cost-effective solution for generating high forces.

The rate at which a test is performed can have a significant effect on tensile properties. Tensile properties for plastics, polymers and steels are very sensitive to testing rates, but aluminum alloys exhibit little sensitivity.

Wedge action grips are the most common style used in metals testing. As the axial load increases, the wedge acts to increase the squeezing pressure applied to the specimen. Wedge grips are manually, pneumatically or hydraulically actuated. For high-volume testing, it is recommended that pneumatic or hydraulic actuated grips be used [10].

3.5.2 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a two-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm) [11].

3.5.2.1 Working Principle

Fig. 3.4 shows the shematic for working of a typical SEM. An electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. The electron beam, which typically has an energy ranging from a few hundred eV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the *x* and *y* axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors.

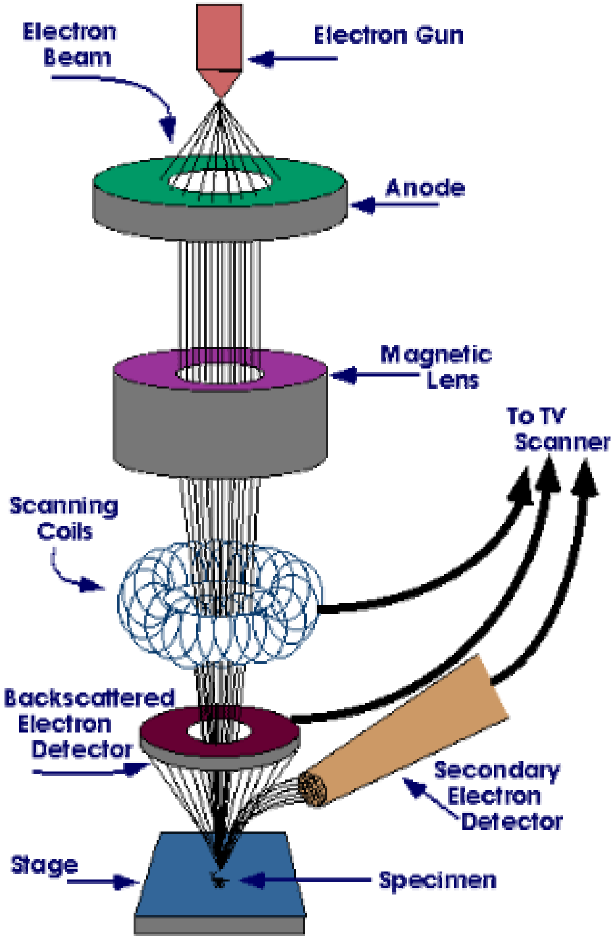


Fig. 3.5- Schematic for working of SEM

The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disc.

3.5.2.2 Sample Prepration

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Two important reasons for coating, even when there is more than enough specimen conductivity to prevent charging, are to maximise signal and improve spatial resolution, especially with samples of low atomic number (Z). Broadly, signal increases with atomic number, especially for backscattered electron imaging. The improvement in resolution arises because in low-Z materials such as carbon, the electron beam can penetrate several micrometres below the surface, generating signals from an interaction volume much larger than the beam diameter and reducing spatial resolution. Coating with a high-Z material such as gold maximises secondary electron yield from within a surface layer a few nm thick, and suppresses secondary electrons generated at greater depths, so that the signal is predominantly derived from locations closer to the beam and closer to the specimen surface than would be the case in an uncoated, low-Z material [12].

3.5.3 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned [13].

3.5.3.1 Working Principle

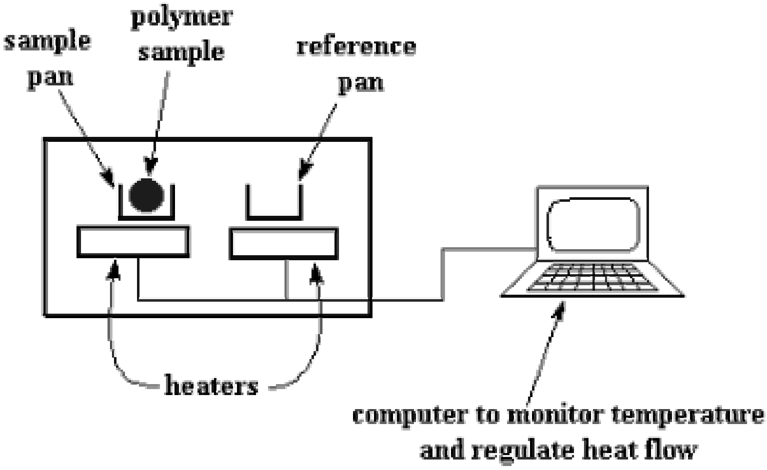


Fig. 3.6 - Schematic showing the principle of DSC

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer properties.

The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity [14].

3.6 References

1. A. Bhatnagar, “Lightweight Ballistic Composites”, Woodhaed Puublishing Lim., 197-198, (2006).
2. www.mth.uea.ac.uk
3. W.F. Smith, “Principles of Materials Science and Engineering”, McGraw-Hill Publishing Co., 2nd ed.,1990).
4. A.Ziabcki, "Fundamentals of Fiber Formation”, John Willey, (1976).
5. E.S. Clark, L.S. Scott., Polym. Eng. Sci., **14**, 682, (1974).
6. J. Smoke, J.C.M. Torfs, A.J. Pennings, Macromol, **182**, 3351, (1981).
7. J.C.M. Torfs, A. van Ekenstein, A.J. Pennings, Eur. Polym. J., **17**, 157, (1981).
8. A.J. Pennings, R.J. van der Hooft, A.R. Postema, W. Hoogsteen, G. ten Brinke, Polym. Bull., **16**, 168, (1986).
9. W. Hoogsteen, G. ten Brinke, A.J. Pennings, Coll. Polym. Sci., **266**, 1004, (1988).
10. www.matweb.com/reference/tensilestrength.aspx
11. www.serc.carleton.edu./techniques/SEM.html
12. G. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. Fiori, E. Lifshin, “Scanning electron microscopy and x-ray microanalysis”, Plenum Press, (1981).
13. P. Erno, “A Practical Guide to Instrumental Analysis” Boca Raton,181-191. (1995).
14. M.E. Brown, “Introduction to Thermal Analysis”, Chapman & Hall, 23-28, (1988).

CHAPTER 4

RESULTS AND DISCUSSION

High strength ultra high molecular weight polyethylene (UHMWPE) fiber is produced by hot-drawing of the as-spun fiber to very high draw ratios. Therefore, the drawability of the fiber is controlled by both the properties of as-spun fiber and drawing conditions. The effects of draw ratio or draw stress and as-spun fiber diameter on the mechanical, morphological and thermal properties are investigated.

4.1 Gel spun/Hot drawn UHMWPE Fibers

From gel-spinning, gel-fibers of two different sizes are produced by using single hole conical dies having exit diameter of 3 mm and 1.4 mm respectively. These fibers are drawn to various draw ratios by multi - stage hot drawing process.

Continuity of the drawing process is determined by the homogeneity of gel spun fibers to a large extent. Variation in diameter, polymer concentration and orientation and inclusion of impurities in gel spun fiber are main reasons for inhomogenity. Accordingly, the probability of fracture at high stresses was decreased by carrying out drawing experiments on a relatively short section of each spun fiber [1].

For this work, the hot drawing temperature is maintained at 110 ºC for both types of fibers. Temperature higher than that will result in breakage of fiber during the process of hot drawing due to burning effect. On the otherhand when drawing temperature is less than 110 ºC, low draw ratio fiber will be produced because fiber has not attained its softening point. The time to reach the required temperature of 110 ºC to the centre of fiber has been calculated by eq.3.1 in experimental section. Depending on this residence time, the feed-up and take-up speeds are tuned accordingly for fibers of 3 mm and 1.4 mm diameters.

The draw ratio for each fiber was calculated by measuring the diameter of fiber before and after drawing. As volume remains constant, therefore draw ratio;

$$\text{Draw ratio } (L_f/L_i) = (D_i/D_f)^2 \quad \text{------------------- (4.1)}$$

Where;

L_i = Length of un-stretched fiber

L_f = Length of stretched fiber

D_i = Diameter of un-stretched fiber

D_f = Diameter of stretched fiber

4.2 Mechanical Properties

Table-4.1 and Table-4.22 summarize the mechanical properties of spun/hot drawn UHMWPE fibers obtained using spinning orifices of 3mm and 1.4 mm in diameter respectively. Higher draw ratios in these experiments are achieved by stretching the fibers repeatedly in hot tube (i.e. more than one time)

Table-4.1- Properties of hot drawn UHMWPE fibers (gel-spun from 3 mm orifice)

UHMWPE Fiber Sample ID	D_i (mm)	D_f (mm)	Draw Ratio	Tensile Strength (MPa)	Young's Modulus (MPa)
1-A	3	1.50	4	97	802
1-B	3	1.15	7	131	1191
1-C	3	0.95	10	186	1761
1-D	3	0.75	16	302	2487
1-E	3	0.60	25	446	3628

Table- 4.2- Properties of hot drawn UHMWPE fibers (gel-spun from 1.4 mm orifice)

UHMWPE Fiber Sample ID	D_i (mm)	D_f (mm)	Draw Ratio	Tensile Strength (MPa)	Young's Modulus (MPa)
2-A	1.4	0.45	10	233	2219
2-B	1.4	0.35	16	375	3312
2-C	1.4	0.30	25	502	4123
2-D	1.4	0.25	30	586	4648
2-E	1.4	0.22	40	790	5785

Stress-strain behaviour of these fibers at various draw ratios, determined by Hounsfield – H10KS tensile testing equipment is shown in Fig. 4.1 and Fig. 4.2. The strength of a fiber is calculated form the force at which the fiber breaks, as it is recorded by the tensile tester, divided by the cross-sectional area of this particular fiber. The cross-sectional area is calculated from the weight of the fiber and the density (970 kg/m^3).

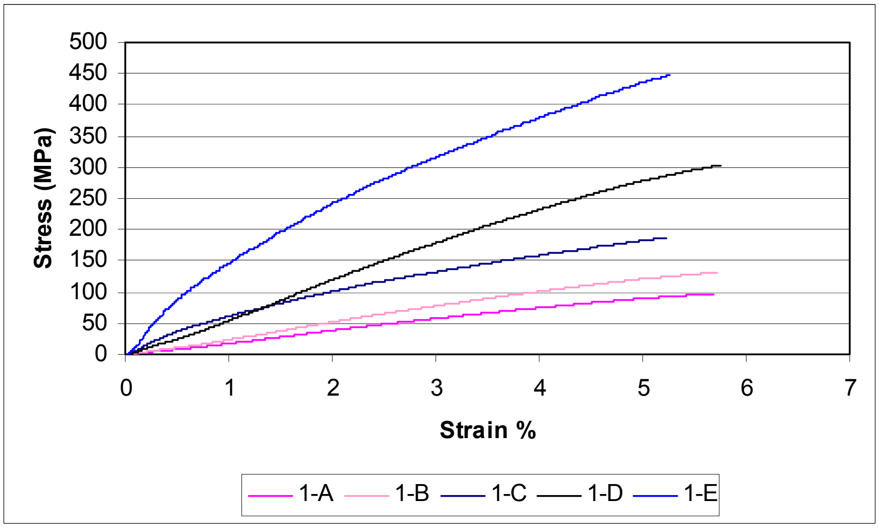


Fig. 4.1- Stress- Strain behaviour of hot-drawn UHMWPE fibers (gel-spun from 3 mm orifice) at various draw ratios

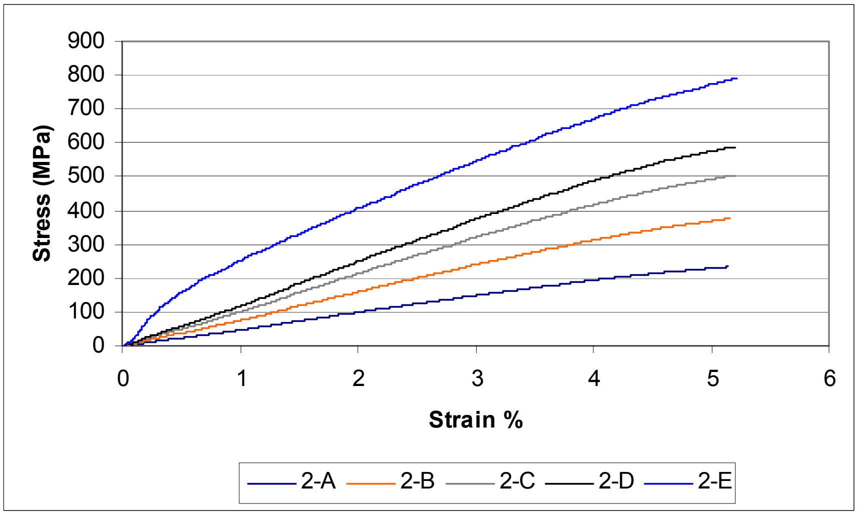


Fig. 4.2 - Stress- Strain behaviour of hot-drawn UHMWPE fibers (gel-spun from 1.4 mm orifice) at various draw ratios

4.2.1 Effect of Draw Ratio

It appears from Fig.4.3, that the tensile strength of UHMWPE fiber is increased by increasing the draw ratio or draw stress. This dependence on the draw ratio might lead to the following interpretation of the drawing mechanism. It is assumed that a certain fraction of the fiber's cross-section is taken up by load-carrying tie molecules that are all ruptured before the fiber breaks [2,3]. This implies that absolute number of load carrying chains in the fiber cross-section, created in the drawing process, is about the same for a fiber with low draw ratio as it is for fiber with high draw ratio. Since the cross-sectional area of a drawn fiber progressively decreases with increasing draw ratio, this number of load carrying chain is confined to a smaller cross-section in fibers with higher draw ratio which is expressed as an increasing tensile strength with increasing draw ratio.

In order to explain the observed tensile force at break behaviour, we will have to deal with the formation of load-bearing tie molecules in the course of the drawing process. This process basically involves the deformation of transient entanglement network, giving a fiber of complex morphology. The formation of load carrying chains will be closely related to the orientational changes that are induced by the elongational flow field in the drawing process [4]. Moreover with increasing draw ratio, the stress also increases the rate of creep and thus the rate of migration of defects (entanglements, intertwinings, chain ends and loops) leading also to the formation of crystals of high perfection [5].

In Fig. 4.4, the Young's modulus of the hot drawn fiber is plotted as a function of draw ratio. The modulus-draw ratio data can be interpreted in terms of a simplified model, proposed by Irvine and Smith, that accounts for the increase of Young's modulus that is observed upon drawing. According to this model, the partially oriented fiber consists two types of elastic elements, viz. perfectly oriented and completely un-oriented elements. Drawing of the fiber results in an increase in the fraction of the perfectly oriented material at the expense of the fraction of un-oriented material. The overall modulus of this composite fiber structure is therefore directly related to the moduli of the oriented and un-oriented phases [6].

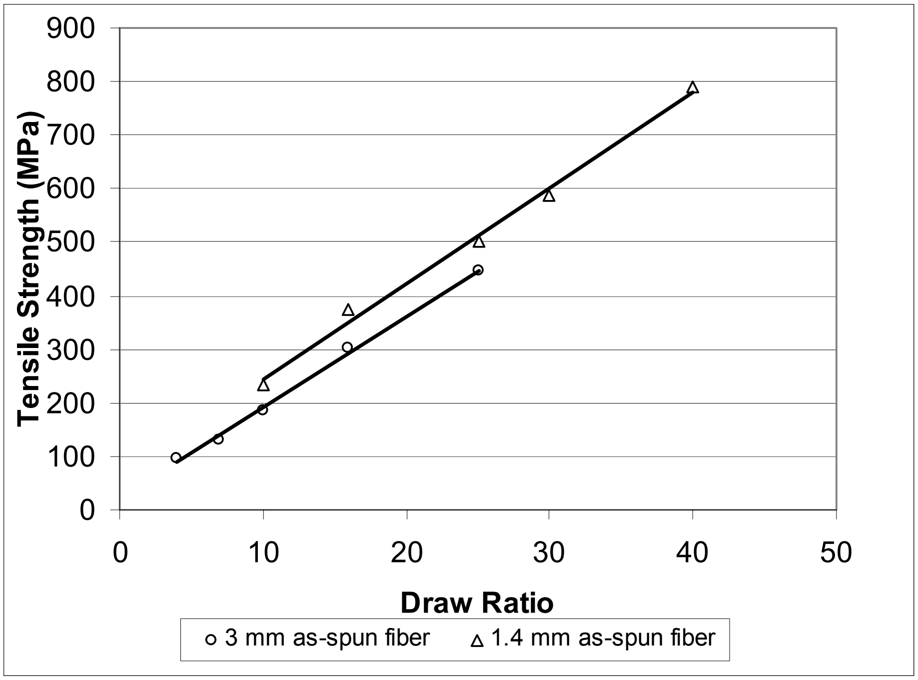


Fig. 4.3- Effect of draw ratio on tensile strength of UHMWPE fiber

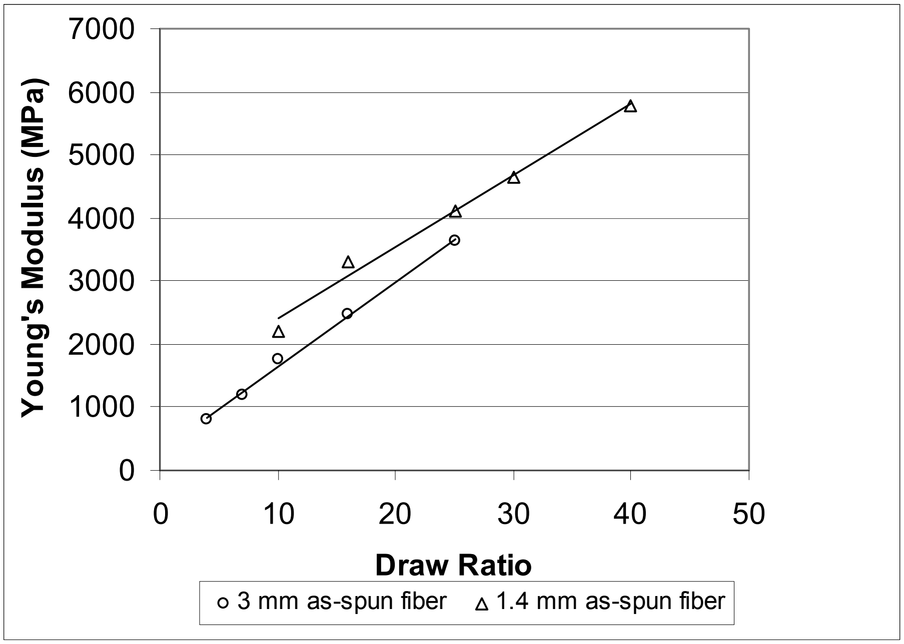


Fig. 4.4 - Effect of draw ratio on Young's modulus of UHMWPE fiber

4.2.2 Influence of Fiber- diameter

The hot drawing more effectively enhances the fiber mechanical properties as the diameter of the undrawn, as-spun fiber is smaller. Fig. 4.3 and Fig. 4.4 show the effect of draw ratio on the of tensile strength and Young's modulus of fibers obtained using spinning orifices of 3 mm and 4.1 mm in diameter. In Fig. 4.3, it can be seen that, at given draw ratio, thinner fibers are substantially stronger than thicker ones, suggesting a pronounced effect of the fiber diameter on tensile strength. However, the Young's modulus is found to depend on the diameter of the fiber as well (see Fig. 4.4). The Young's modulus reflects a number of structural properties of the fiber, such as the degree of chain orientation and the fraction of load carrying chains.

Therefore it follows from our data that fiber structure develops more efficiently during hot-drawing as the diameter of the undrawn precursor fiber has a smaller diameter. These effects are remarkably pronounced, especially at higher draw ratios. For example, at a draw ratio of 25, fibers prepared from the 1.4 mm as-spun fiber have strength and modulus of 502 MPa and 4143

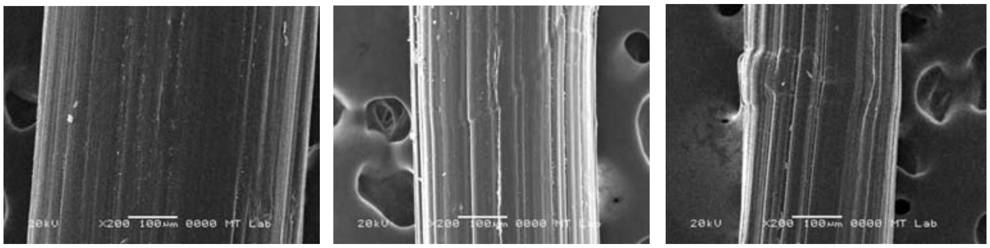
MPa respectively, whereas fibers prepared from the 3 mm precursor have an average strength and modulus of 446 MPa and 3628 MPa respectively.

It is concluded from the above mentioned results that, at given draw ratio, moduli and strength are remarkably higher when the undrawn fiber is thinner because the number of chains (per unit area) that becomes extended have a higher fraction of load carrying chains.

4.3 Morphology

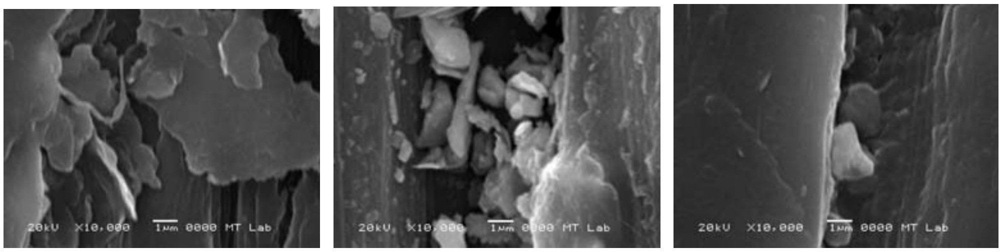
4.3.1 Influence of Draw ratio

Fig 4.5 and Fig 4.6 present low and high magnification SEM micrographs of the hot-drawn UHMWPE fiber specimens, respectively. As shown in Fig 4.5a - c, at higher draw ratios, more aligned chains with considerable reduction in striation width can be seen which is due to the easy chain slippage through the entanglement network, suggesting an increase in extended chain molecules that span the amorphous domain. It can be concluded from Fig. 4.5a-c that lamellar portion reduces and fibrillar region increases significantly as the D.R. values increase from 10 to 25. Fig 4.6 shows the clear cut amorphous and crystalline region. It is observed from results presented that an increase in draw ratio would enhance the crystalline region at the expense of amorphous region by the mechanism of molecular orientation and hence increases the tensile strength and modulus of fiber. Moreover, stored elastic strain exerts to cause fiber deterioration which is more evident at draw ratio of 10 (see Fig 4.6a) but at higher draw ratios this fiber degradation is reduced more efficiently due to diminution in stored elastic strain energy by the easy chain movement (see Fig 4.6c)



(a) (b) (c)

Fig. 4.5- Low-magnification SEM micrographs of the UHMWPE fibers (as-spun diameter of 3 mm) with D.R. values of (a) 10, (b) 16, and (c) 25



(a) (b) (c)

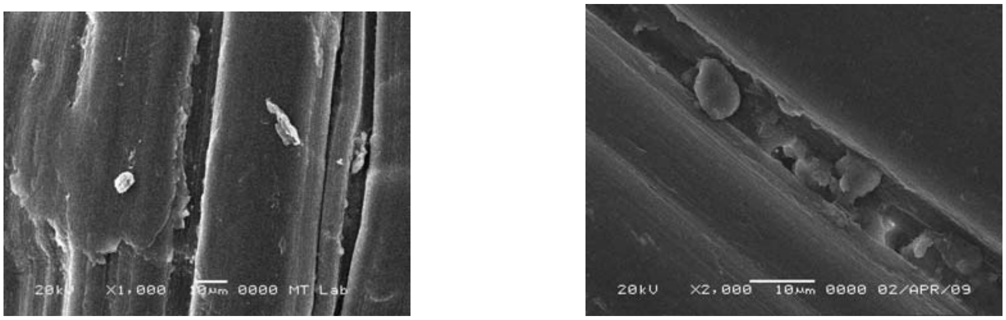
Fig. 4.6- High-magnification SEM micrographs of the UHMWPE fibers (as-spun diameter of 3 mm) with D.R. values of (a) 10, (b) 16, and (c) 25

Upon hot drawing, the lamellae in the as-spun fiber are transformed into fibrillar crystals. This structural rearrangement is apparently accompanied by an increase of the tensile force at break of the drawn fiber. This is not surprising, however, since this process increases the number of chains that are aligned along the fiber axis. It is concluded that no substantial slip of chains through entanglement hooks occurs at lower draw ratio. Initially, only one-third of the network chains transmit forces in the fiber direction and consequently only one-third of the network chains will be extended between the entanglement points [7]. At higher draw ratios, the slippage of chains through the hooks formed by entanglement becomes predominant, as it is reflected in a much higher increase in crystalline region.

4.3.2 Effect of Fiber- diameter

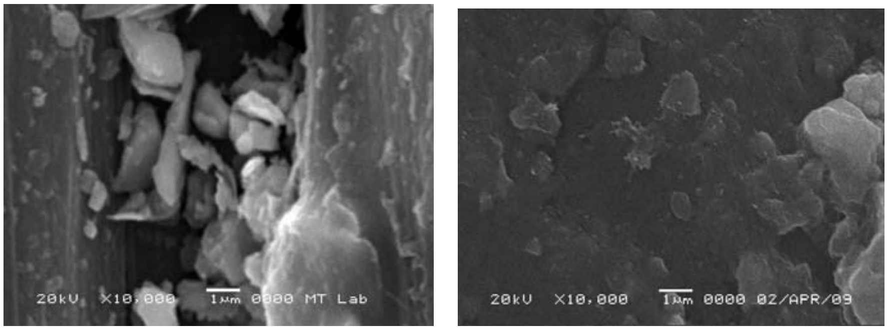
The hot drawing more effectively improves the fiber morphological properties as the diameter of the undrawn, as-spun fiber is smaller. Fig. 4.7 and Fig.4.8 show the typical low and high magnification SEM micrographs of fibers obtained using spinning orifices of 3mm and 1.4 mm in diameter respectively. It is observed from the Fig. 4.7 that when the as-spun fiber diameter is small, the striation width decreases effectively due to increase in chain slippage. Consequently this chain slippage enhances the transformation from lamellae to fibrillar in the fiber. At higher magnification (see Fig.4.8), it can be seen that the degradation of fiber is more pronounced in case of as-spun thicker fiber as compared with thinner fiber.

This behaviour can be explained in terms of thermal gradient present in fibers during the course of hot-drawing process. Due to the low thermal conductivity of polyethylene, amount of thermal gradient in thicker fiber is much higher as compared with thinner fiber. Therefore thicker fibers are gradually heated up from outside while the temperature at core of fiber has not reached to the desired value. In the presence of this thermal gradient, when such fiber is hot drawn to various draw ratios, the mechanism of chain slippage starts preferably at outer layers of the fiber. The inner layers of fiber which has not reached the softening point will be degraded due to exertion of stored elastic strain from outer layers. As it can be seen in Fig.4.8 b, this effect is remarkably reduced in case of thinner fiber due to better homogenization of thermal effects. Consequently, the fibrillar region is increased by reducing the thermal gradient in UHMWPE fibers by producing less diameter as-spun fiber which will further enhance the physical and mechanical properties of the fiber.



(a) (b)

Fig. 4.7- Low-magnification SEM micrographs of the UHMWPE fibers (at D.R. of 16), (a) as-spun diameter of 3 mm (b) as-spun diameter of 1.4 mm



(a) (b)

Fig. 4.8- High-magnification SEM micrographs of the UHMWPE fibers (at D.R. of 16) (a) as-spun diameter of 3 mm (b) as-spun diameter of 1.4 mm

4.4 Thermal Analysis

Fig. 4.9 shows the DSC thermograms of UHMWPE fibers drawn at two different draw ratios from as-spun fiber of 3 mm diameter. It can be seen that at draw ratio of 10, melting peak is at 127.37 ºC. For draw ratio of 25 this peak shifts to the temperature of 138.60 ºC and becomes slightly sharper. Almost the same behaviour can be observed in Fig. 4.10, showing the DSC thermograms of two hot-drawn fibers at the same draw ratio but gel-spun using die orifices of 3mm and 1.4 mm in diameter. In this case, it is quite evident that by reducing the as-spun fiber thickness, a slight shift to the temperature and peak sharpening is observed.

This shift in melting temperature and peak sharpness results from the transformation from a lamellar to fibrillar morphology, which is accomplished by an effective extension of macromolecules between entanglements. For thinner fiber, due to better thermal distribution in the course of hot drawing, more transformation takes place due to the easy chain-slippage and less fiber deterioration. Whereas in case of thicker fiber, hot drawn at the same draw ratio as thinner fiber, the transformation from lamellar to fibrillar is less due to the presence of thermal gradient and stored elastic strain energy which exerts to deteriorate the fiber. It is assumed that amount of fibrillar material present may be correlated to the crystallinity of the fiber.

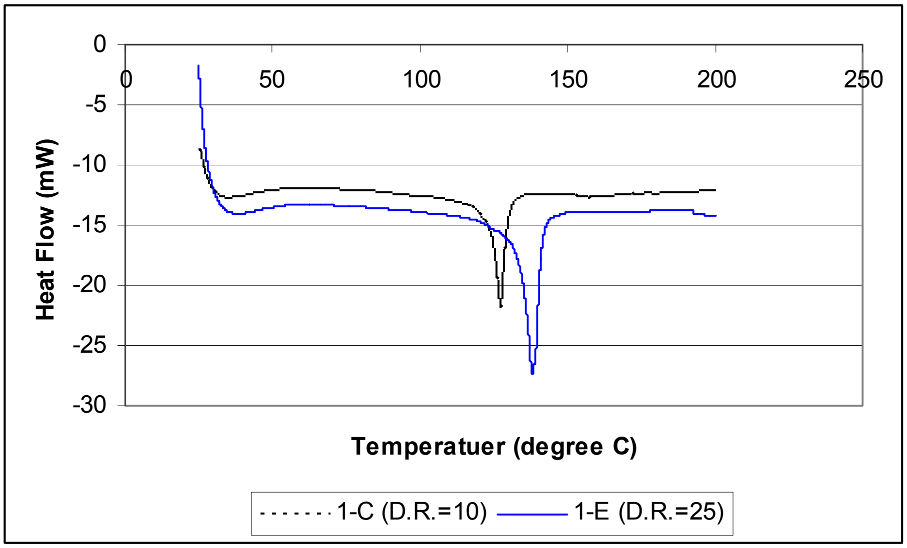


Fig. 4.9- DSC thermograms of hot drawn UHMWPE fiber specimens (gel-spun from 3 mm orifice) with draw ratios of 10 and 25

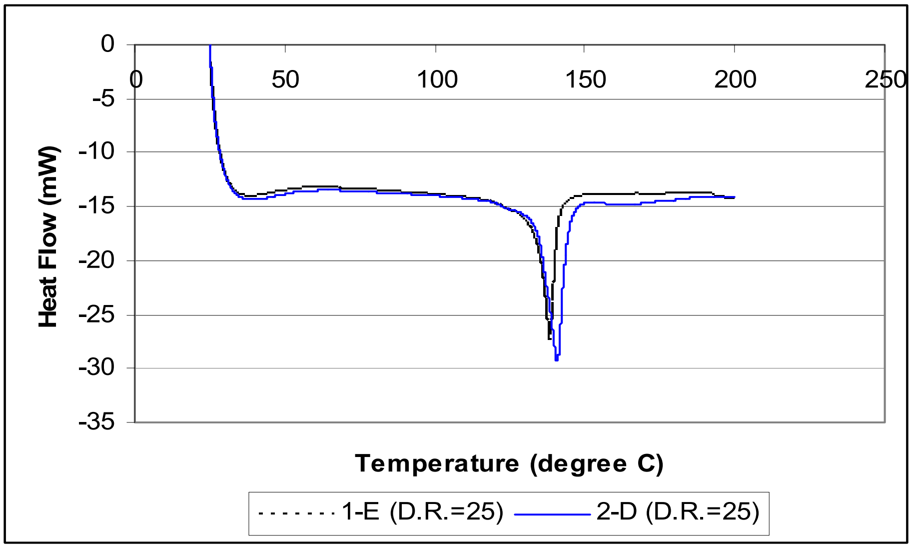


Fig. 4.10- DSC thermograms of hot drawn UHMWPE fiber specimens at draw ratios of 25 (gel-spun from 3 mm and 1.4 mm orifices)

4.5 Role of Entanglements in Drawing Process

The low tensile strength and modulus of un-oriented UHPWPE is due to presence of chain folded crystalline and amorphous structure. Entanglements play very important role in drawing mechanism. To highly orient the molecules it is very essential to remove the entanglements. In hot drawing experiments, slippage of chins through entanglement hooks becomes predominant, when maximum network draw ratio is exceeded. These slippage events allow elongation of the molecular strands, oriented in the fiber direction through the entanglement hooks. This process reduces the fiber diameter and increases its length, while the number of the number of chains that transmit forces in the fiber direction remains constant. Since elongation of the fiber proceeds through slippage, rather than breakage of load carrying chains, this process will be accompanied by migration of entanglements, that are acting as 'slip-links' [1]. Fig. 4.11 represents the schematic for stretching of an entanglement network into the oriented structure. The maximum attainable draw ratio is likely to be limited by the accumulation of entanglements in complex topological defects, and tight knots, which cannot be removed upon drawing.

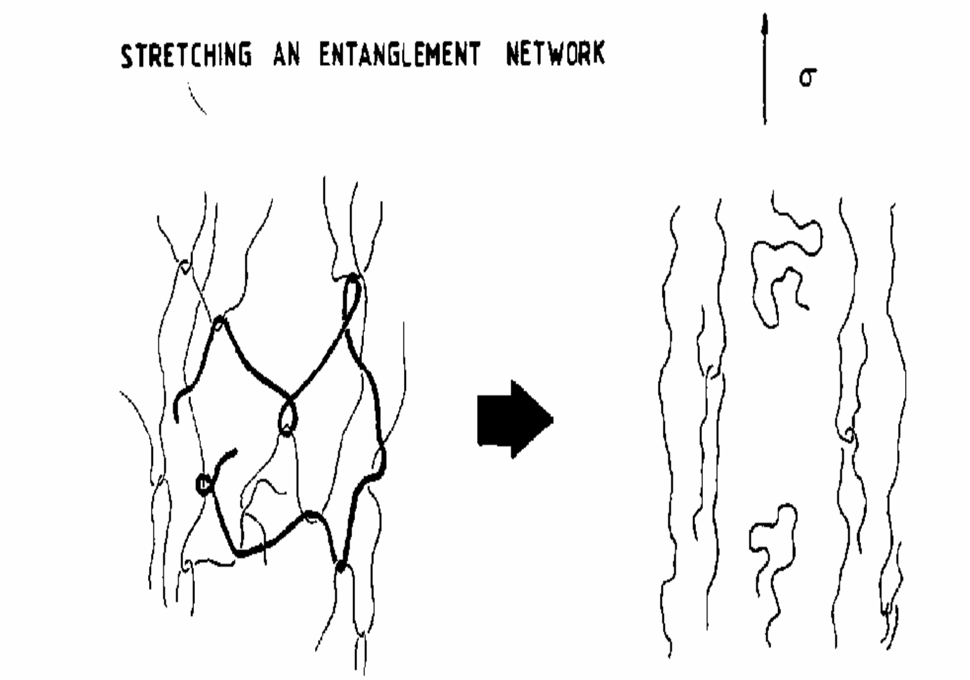


Fig. 4.11 - Schematic representation of stretching of an entanglement network

4.6 References

1. B. Kalb, A.J.Pennings, *J. Mater. Sci.,* **15,** 2584-2590, (1980).
2. A. Peterlin, Polym.Eng. Sci., **19**, 118, (1979).
3. J.P. Penning, H. van der Werff, M. Roukema, A.J. Pennings, Polym. Bull., **23**, 347, (1990).
4. Y. Termonia, P. Smith, Macromolecules, **21**, 2184, (1988)
5. B. Kalb, A.J. Pennings, Polymer,**1,** 871-876, (1979).
6. P.A. Irvine, P. Smith, Macromolecules, **19**, 240, (1986).
7. F. Bueche, “Physical Properties of Polymers”, Interscience, 237, (1962).

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Comparison of Mechanical Properties

The mechanical properties of UHMWPE fiber produced in this experimental work and commercially available fiber are compared in Table 5.1 [1]. The low tensile strength and modulus values of experimental fiber in our work are primarily due to the low molecular weight of polymer. Since high molecular weight polymers have high elongational melt viscosities, the stress during the drawing is also very high, which will enhance the molecular elongation and improve the orientation and the mechanical properties of the fibers [2].

Table 5.1- Comparison of Mechanical Properties of UHMWPE Fibers

UHMWPE Fiber	**Molecular Weight** (g/mol)	**Strength (GPa)**	**Modulus (GPa)**	**Strain at break (%)**
Spectra 1000	4.5 x10^6	3.0	172	3.5
Fiber in this experiential work **(2-E)**	1.0 -1.5 x10^6	0.790	5.785	5.2

5.2 Conclusions

Hot drawing of ultra high molecular weight polyethylene (UHMWPE) fibers is controlled by number of factors; molecular weight, degree of polymerization, gel concentration, as-spun fiber diameter, length of drawing tube, drawing temperature, and draw ratio or draw stress. Mechanical, morphological and thermal properties of UHMWPE fibers are found to be significantly influenced by the as-spun fiber diameter and draw ratio or draw stress.

The draw ratio has direct effect on the tensile strength and Young's modulus of the fiber. Ultra high molecular weight polyethylene fiber of high strength and modulus is produced by applying higher draw ratio or draw stress. Whereas chain extension in hot drawing and the ultimate draw ratio depend on the number of intermolecular entanglements initially present in the fiber. The higher number of entanglements makes it necessary to apply a much higher stress in order to remove the entanglements and achieve the maximum strength. In hot drawing experiments, slippage of chains through entanglement hooks becomes predominant at higher network draw ratios. These slippage events allow elongation of the molecular strands, oriented in the fiber direction, at the expense of remaining material. This process reduces the fiber diameter and increases its length, while the number of chains that transmit forces in the fiber direction remains constant, resulting in higher strength of fiber.

The increase in draw ratio, results in higher fraction of perfectly oriented molecules as compared with completely un-oriented molecules. There is pronounced degradation of fiber at lower draw ratio, due to the difficult chain-slippage. The more fibrillar and crystalline fiber with enhanced mechanical properties is obtained at higher draw ratio.

Further, at given draw ratio, moduli and strength are remarkably higher when the undrawn fiber is thinner because the number of chains (per unit area) that become extended have a higher fraction of load carrying chains. Due to low thermal gradient for thinner fiber, chain slippage is much easy as compared with thicker fiber. Consequently, the fiber degradation is less and transformation from lamellae to fibrillar is higher. Moreover the transformation from amorphous to crystalline material is also enhanced due to the better homogenization of thermal effects in the fiber. All these factors contribute to the fiber having good morphological properties along with higher tensile strength, modulus and crystallinity.

Further, the formation of neck during hot drawing apparently leads to low value of tensile strength. Therefore in order to achieve continuous and ultra strong fibers, the conditions for drawing have to be adjusted so that the formation of neck can be prevented

Finally, we reach at the conclusion that ultra high molecular polyethylene (UHMWPE) fiber with better physical and thermal properties and high strength, modulus and cystallinity is produced by employing as-spun fiber of smaller diameter and conducting hot drawing process at higher draw ratio.

5.3 Future Work

It is quite obvious from the present work and its results that there are some areas which still need to be addressed to improve the physical, mechanical, thermal and morphological properties of UHMWPE fibers to use them as reinforcing to develop highly impact resistant armor/ballistic composite materials. Following are some of the suggestions for future works to be done:

1. The use of ultra high molecular weight polyethylene (UHMWPE) with molecular weight of up to Mw= 4.5 x10^6 g/mol (Mw= 1.0 -1.5 x10^6 g/mol in present work) to produce fibers with higher strength and modulus.
2. To produce the UHMWPE fiber having diameter less than 1mm from gel spinning process.
3. The thermal homogenization of UHMWPE fibers by dispersing with nano-particles.
4. Impregnation of these high strength fibers with suitable resin to produce armor ballistic composite material.
5. Evaluation testing of the composite armors through a variety of techniques including impact testing, dynamic testing and shockwave testing.

5.4 References

1. B. Kalb, A.J.Pennings, *J. Mater. Sci.,* **15,** 2584-2590, (1980).
2. K. Tashiro, M. Kobayashi, H. Tadokoro, Macromol., **11**, 914, (1978).