THE PREPARATION AND PROPERTIES OF HIGH PERFORMANCE POLYETHYLENE STRUCTURES

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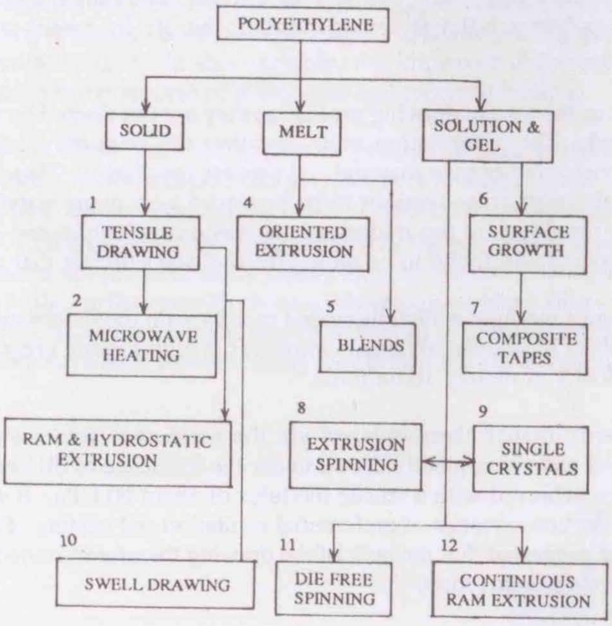
Introduction

In the last fifteen years numerous studies have been made with the view of manipulating long polymer molecules so that the final mechanical properties of the material could be enhanced and this is reflected by numerous publications and patent applications on the subject. A number of these processes which employed the three basic routes namely, the solid state process, melt processing and solution state processing have been shown to be relatively successful. These techniques together with the new techniques developed by this author are shown schematically in Figure 1. The resultant mechanical properties are shown in Figure 2.



1 & 3 Ward et. al.
2 Konaka et. al.
4 Keller et. al. & Porter et. al.
5 Keller et. al.
6 Pennings et. al.
7 Mackley et. al.
8 Lemstra et. al. & Pennings et. al.
9 Kanamoto et. al.
10, 11 & 12 New Methods

Figure 1 Development of High Performance Polyethylene Manufacturing Techniques.

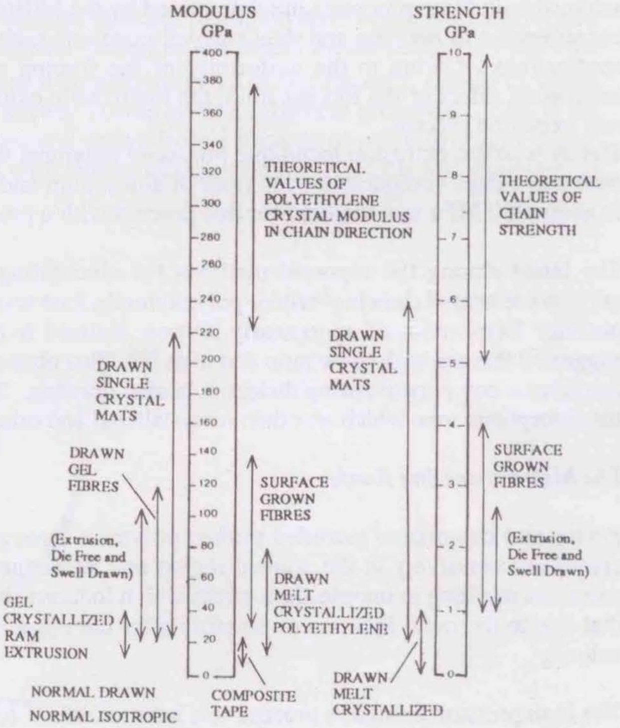


Figure 2 Tensile Moduli and Strengths of Polyethylene. Prepared by the different techniques shown in Figure 1.

The Solid State Processing Route

The simplest method of orienting some polymer molecules is by physically stretching the workpiece and this process is called the tensile drawing process[1] and was developed as a result of the optimization of the cold drawing phenomenon. *Andrews* and *Ward* [2] observed that the elastic modulus of polyethylene increased from about 1 to 23 GPa monotonically with draw ratio. Polyethylene of various grades were used with each specimen drawn to its natural draw ratio; where draw ratio is defined as the final stretched length divided by the original specimen length. An important observation made was that whilst the final strength attained increases with molecular weight and the elastic *Youngs* modulus also increases with draw ratio; the polymer drawability was found to decrease with increasing molecular weight[3]. This seemed to suggest that the presence of long molecules, with more entanglements, inhibited the drawing process and prevented the attainment of high moduli. It follows that by this route, strength and elastic modulus may be obtained one at the cost of the other.

Capaccio and *Ward*[4] showed that by maintaining the tensile draw temperature above ambient but still well below the melting point of the polymer, the production of microvoids was minimised and at the same time prevented the onset of *flow drawing*. In this manner, a polyethylene with M_w = 6900 was drawn to an oriented monofilament giving a room temperature *Young's* modulus of 40 GPa for a draw ratio of 20. They suggested from their experimental results that very high draw ratios and *Young's* moduli may be achieved with linear polyethylene provided that the structure of the undrawn material and the drawing process itself were fully optimized. In all of the work reported by *Ward* and coworkers[1-4,] the stiffness of the polymer was found to be proportional to the final draw ratio and for polyethylene a modulus of 70 GPa was achieved for a draw ratio of around 30. The tensile drawing process established the observation that high strengths and high moduli are achievable by tensile extension to high draw ratios. However, it was discovered that the tensile drawing process was limited by material factors and process mechanics such as polymer morphology, drawing temperatures and drawing rate. The maximum draw ratio obtainable from the tensile drawing processes was also limited by the fact that the uniaxial tensile force resulted in the instability due to necking and the subsequent stress concentrations in the polymer which gave rise to premature material failure.

The problems of necking and inhomogeneous extension were overcome to a certain extent by the hydrostatic and ram extrusion processes. The former being a process which was borrowed from a technique familiar in the plastic forming of metals and entails forcing a polymer billet through a convergent die by applying pressure to a fluid. The ram extrusion process is similar to the hydrostatic extrusion except that the polymer billet is forced through the die by means of a mechanical piston.

The hydrostatic and ram extrusion processes have an advantage over the tensile drawing process as they are not limited by the constraints previoulsy mentioned for the tensile drawing method. The deformation ratio, and thus the final draw ratio, achievable in these processes are determined by the billet-die geometry rather than material and process mechanics. They are not subjected to necking and thus enabled materials with relatively large cross-sections to be produced with many possible applications. Owing to the uniformity of the forcing pressure provided by the hydrostatic extrusion technique and the lubricating effect of the forcing fluid, the hydrostatic extrusion process was found to be more effective and efficient than the ram extrusion process.

The hydrostatic extrusion technique produced polymers with *Young's* modulus which increased rapidly with the deformation ratio and values comparable with those of aluminium and glass fibres have been obtained. However, a high forcing pressure or about 200 MPa was required for this process with a product velocity of merely 10 mm/min.

The latest among the reported methods for elucidating high performance thermoplatics via the solid state route is the microwave heated drawing[5] where polyoxymethylene was extruded and subsequently drawn under the influence of dielectric heating. Draw ratios of up to nearly 30 were claimed to have been achieved with a tensile modulus of about 60 GPa. It was suggested that the high draw ratio and high modulus obtained was the consequence of preferential excitation and heating of the amorphous component during dielectric heated drawing. They also suggested that the bulk of the drawing therefore occured in the amorphous zone which was then recrystallized and oriented in the draw direction.

The Melt Processing Route

Porter and coworkers[6] extruded molten polymers through a conical die at very high pressures by allowing the polymer to crystallize *massively* in the conical region and subsequently forcing it into the relatively narrow diameter die capillary by pressures resulting in intense shear stress which induced an oriented and extended crystal structure. However, it was discovered that due to the rapid increase of pressure after the onset of crystallization it was impossible to maintain a constant extrusion velocity[7].

The high pressure extrusion process was later modified[8] to reduce shearing and the associated strain hardening without the use of lubricants. This was achieved by the introduction of longitudinal free surface areas in the extruded bilets (by splitting) of preformed morphology and pulling the extrudate during the process of extrusion. It is suggested in the former case that stresses which would normally develop during the extrusion of a conventional unsplit billet are changed and relieved. Admittedly, this process in its modified form, has essentially become a solid state process.

Another development in the melt route is that reported by *Odell*, *Grubb* and *Keller*[9] where oriented plugs (or short fibres) or polyethylene about 50mm long and 0.8mm diameter were produced. This was achieved by extruding polyethylene just above the melting point through a capillary and blocking the die exit with a needle valve at a critical temperature and flow velocity, thereby causing crystallization of the melt in the die due to the rapid rise in pressure. More recently, *Bashir*, *Odell* and *Keller*[10] used the same technique in blends of high and normal molecular weight polymer and reported that the oriented extrudate obtained exhibited improved mechanical properties even if only small amounts of very high molecular weight components were present. The longest chains procuced fibrous crystals during extrusion which were inadequate to influence the properties in themselves. The however served as nuclei for lamellar crystallization and determined the detailed arrangements and hence the mechanical effectiveness of the lamellar texture.

The Solution Processing Route

Even though the tensile drawing technique is useful and effective for low to normal molecular weight polymers and is widely utilised in industrial production of films and tapes[11] at present it appears ineffective for polymers with very high molecular weight[12] . The main reason for the dependence of polymer drawability, and hence the maximum stiffness obtained, on the molecular weight of the polymer is that the longer the polymer chains the more entangled are the network and hence it is more difficult for the polymer to deform plastically.

The ability to process very high molecular weight polymers is essential if strength is a major criterion. However, the zero shear viscosity of molten polymers increases with molecular weight, M_w, by the relation $\eta=(M_w)^n$, where n=3.4[13], With the increasing value of molecular weight distribution the viscosity of the polymer melt progressively increases and for polyethylene when $M_w > \sim 10^6$ the material becomes essentially underformable by viscous processing procedure. The high molecular weight, and consequent high entanglement concentration also means that the material can only be deformed to a small degree. For these ultrahigh molecular weight polymers there are two possible methods of processing; the first method is by sintering or compression moulding and the second method, which has an added advantage in the production of high performance polyethylene, is by dissolving the polymer in a suitable solvent so that it can be processed easily. The gel spinning processes have been developed to overcome the problems of poor plastic deformabioity in polymers of very high molecular weight. In this example, the improved deformability is achieved through a reduction of entanglements in the polymer via the process of dissolution and recrystallization.

There are three basic techniques of producing high performance polyethylenes from solution which are reported in the literature. At one extreme the polymer is crystallized from solution to form lamellar single crystals which are then formed into a film and subsequently drawn[14] to produce polyethylene structures with *Youngs* modulus and tensile strength of 160 GPa and 4.7 GPa respectively[15]. Alternatively the polymer is crystallized as a continuous array of fibrous *shish kebabs* in which the chains are predominantly highly extended and which themselves already posses good mechanical properties. This is the basis of the surface growth process where polyethylene fibres are seeded and drawn from a solution of polyethylene in xylene in a couette arrangement as shown in Figure 3[16]. Polyethylene fibres with tensile moduli of up to 170 GPa and strengths up to 5 GPa have been reported using the surface growth technique[17].

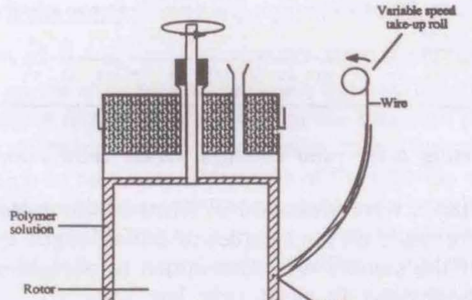


Figure 3 Schematic Diagram of the Couette Apparatus used in the surface growth method of preparing High Performance Polyethylene.

It was soon recognised that this technique proceeds by means of gel stretching at the rotor surface and that the crystallization arise from prestretched molecules[18]. This observation further leads to an adaptation of the surface growth technique for the production of oriented polyethylene films[19]. In this method the growth of the fibres is made to occur on a belt which wraps around but moves in the opposite sense to the rotor. The harvested tapes are reported to posses a highly oriented structure within an unoriented matrix with distinct melting temperatures. It is possible to selectively melt the matrix and by laminating layers of these tapes, a unique composite material, made up of polyethylene fibres in a polyethylene matrix, may be formed in a heated press[20].

Finally, further developments in this field has led to the third and technologically most successful group of methods which involves making the polymer solution, and subsequent extrusion of it to form a fibre[21]. The gel fibre is quenched and allowed to crystallize. It is then dried and drawn to high draw ratios to produce a strong, stiff structure. With this extrusion spinning technique, polyethylene fibres with *Young's* moduli of up to 120 GPa and tensile strengths up to 3 GPa have been obtained.

Swell Drawing of Ultrahigh Molecular Weight Polyethylene

In the continuing effort of seeking alternative methods to produce strong, stiff polyethylenes it was discovered that under certain conditions high drawability can be achieved without resorting to dissolution or fluid processing[22]. The technique relies on starting with a workpiece of a chosen geometrical form; swelling the workpiece in an organic solvent under conditions where dissolution does not occur and then after subsequent cooling, hot drawing the workpiece either uniaxially or in principle biaxially. The method relies on being able to introduce a large quantity of solvent into the workpiece by swelling without allowing dissolution to occur.

The sequence for the preparation method of high performance structures is as follows:

i) Manufacture of precursor workpiece
ii) Swelling
iii) Quenching and recrystallization
iv) Solvent removal
v) Development of anisotropy by drawing

If desired steps 1 and 2 can be combined and steps 4 and 5 fully or partially interchanged.

Figure 4 shows the maximum draw ratio that could be obtained for samples that had been swollen to different levels of weight of the amount of solvent absorbed divided by the weight of the polymer, W_s / W_p. The drawability of the specimens was noted to depend on the residual solvent content in the polymer - freshly prepared specimens had better drawability than those which have been prepared a few days before and special precaution was taken to ensure that for each tensile drawing experiment the specimen was freshly swollen, dried in the JJ^{TM} environmental cabinet for approximately 20 minutes at 80°C and then drawn at the desired temperature.

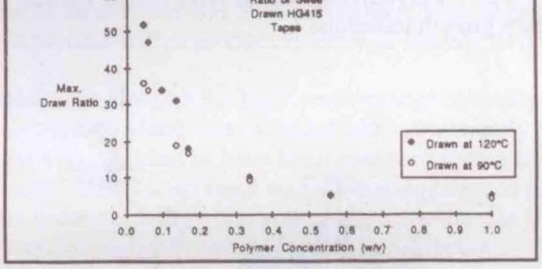


Figure 4 Maximum draw ratio obtained versus Intitial Swelling Ration.

The mechanical properties of the drawn tapes were measured in terms of the room temperature (ca. 20°C) tensile *Youngs* modulus and strength. Measurements were made on the samples of initial length 150 - 200 mm at a crosshead speed of 10 mm/minute. The cross sectional area of the sample was determined by weighing known lengths of test specimen and assuming a density of 1,000 kg/m^3 for polyethylene.

Figures 5 - 7 show the tensile *Youngs* modulus, the tensile strength and the maximum strain respectively for UHMWPE samples that had been drawn to different draw ratios. The familiar progressive increase in properties with increasing draw ratio can be seen together with the fact that a maximum modulus of 102 GPa and strength of 2.4 GPa were obtained. It is felt that these figures are relatively conservative in that as yet the optimization of the drawing conditions which could lead to further improvement in properties is not exhausted. Even though great care was taken, it was impossible not to flex or bend the specimen during removal from the hot grips so that it can be prepared for the subsequent stage of the drawing process. The oriented specimen was observed to be relatively weak in compression and the structure was observed to form kinks when subjected to a flexural strain during bending. Such kinks are regions of structural weakness which could give rise to premature failure. A better method of hot drawing can either be a single - or multi-stage process and one that does not subject the material to undue bending or uniaxial compressive strains.

The anisotropy is developed solely in the drawing process[23]. The enhanced orientation is also relfected in the melting behaviour of the tape which is shown in Figure 8. Figure 8a shows the scanning calorimeter (DSC) trace of a swollen tape drawn to draw ratio of 30X superimposed on a trace of the same sample being remelted. Figure 8b shows the curve for the workpiece swollen to W_s / W_p ratio of 17 and Figure 8c is a DSC trace of the as-extruded and skived tape. All the curves were similar in that the swollen material had a similar trace to the melt processed tape and the drawn material had three characteristics melting peak at 153.5°C, 160.6°C and 166.9°C where the absolute magnitude of the peak temperatures would depend on heating rate.

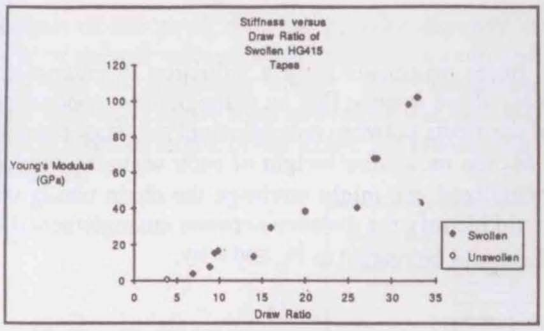


Figure 5 Young's Modulus of Swell Drawn Ultrahigh Molecular weight tapes.

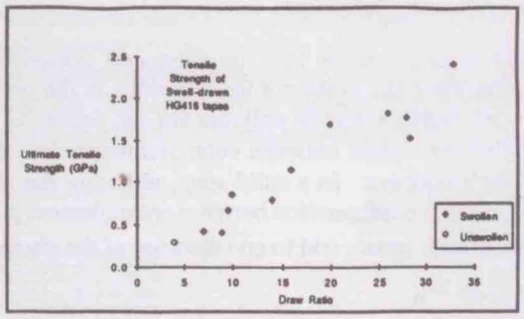


Figure 6 Ultimate Tensile strength of Swell Drawn Ultrahigh molecular weight tapes.

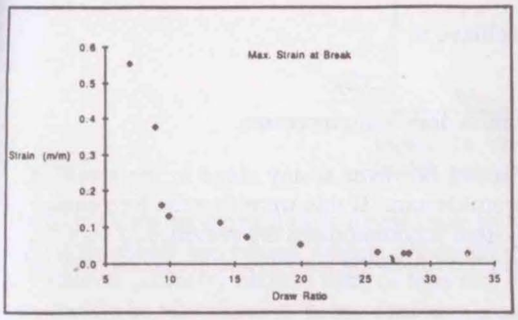


Figure 7 Maximum strain at break of Swell drawn Ultrahigh molecular weight tapes.

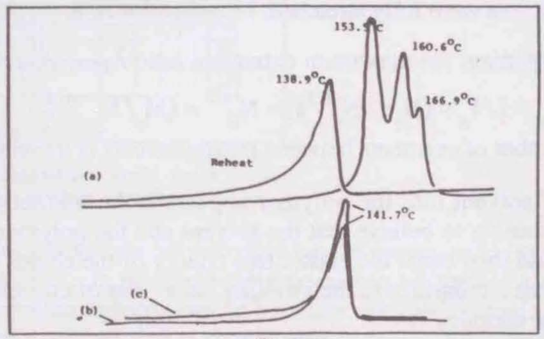


Figure 8 Differential Scanning Calorimeter traces of Swell drawn Ultrahigh molecular weight tapes. Heating Rate 10 deg/min; 2mg sample (a) draw ratio = 30 (b) swollen, dried but undrawn (c) Tape as received.

The transformation of the single peak, normal melting DSC trace of undrawn polyethylene to the triple peak trace of a highly oriented swell drawn material was observed to occur in two stages. The first stage is the shift of the first melting endotherm with increasing draw ratio to a higher temperature until the draw ratio reaches about 20. Figure 9 shows a DSC trace for a swollen material drawn to λ=18 which indicates the beginning of the emergence of the second endothermic peak. It can also be seen that the first peak has shifted from the normal melting temperature of about 138°C to 148.4°C. The third peak appears at a much higher draw ratio in excess of $\lambda = 25$ and these peaks were observed in every specimen drawn to $\lambda > 30$. The reason for this phenomenon is unclear as the experiments have not been sufficiently exhaustive to systematically study the effect of drawing on melting endotherms or the crystal structure of the resultant polymer. One plausible explanation is that it is related to the progress or molecular orientation and rearrangement during drawing. The magnitude of the endothermic peak is a measure of structural integrity which in turn is an indication of the stability of a given molecular structure. As the polymer is drawn, the molecules extend and rearrange themselves in a stable new packing arrangement in order to accomodate the increasing tensile stress during drawing. This is reflected by the increase of the first endotherm. As the extension is further increased some of the molecules will be fully stretched and crystallize in a new equilibrium crystal structure shown by the emergence of the second endotherm peak. The third, and other peaks, may also be brought about by similar processes.

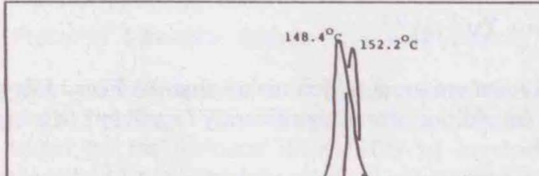


Figure 9 Differential Scanning calorimeter traces of swollen ultrahigh molecular weight tapes (conditions as in Figure 8). Draw ratio (a) 18 (b) 23 (c) 30.

Modelling of drawing behaviour

Smith and *Lemstra* [24] argue that the enhanced drawability of the gel fibres originates from a reduction in entanglement concentration when the precursor gel is cooled in the presence of solvent. If we assume that an entanglement concentration network exists within the solid polymer we dan define N_e the number of segments between entanglement points or equivalent M_c the molecular weight between entanglement points where M_c=N_e M_o the molecular weight of each segment with a the length of each segment. In a solid state, although the chains have crystallized, we might envisage the chain taking up an essentially random configuration between entanglement points and we could identify the distance between entanglement ponits I_o as the root mean square end to end distance of the chain. In this way I_o would be related to N_e and a by,

$$I_o = N_e^{1/2} a \qquad \text{...(1)}$$

In an analogous way to a crosslinked rubber, deformation of the sample can be thought of in tems of deformation of the crosslinked network. The maximum deformation that the network can sustain would then be when the chains between entanglement points were fully stretched, i.e. when $I = N_e a$.

Thus by this argument the maximum extension ratio λ_{max} that the sample can achieve is

$$\lambda_{max} = I / I_o = (N_e a / N_e^{1/2} a) = N_e^{1/2} = (M_c / M_o)^{1/2} \qquad \text{...(2)}$$

Thus as the number of segments between entanglements is increased so the maximum draw ratio increases.

The ingress of solvent into the polymer appears to be a kinetically driven process, however at any stage in the swelling process it is plausible to believe that the solvent and the polymer chains are in quqilibrium. If this were true the free energy of dilution would then equal the elastic free energy of the chains as the binary system accommodates the presence of solvent. This situation has similarities to the swelling behaviour of crosslinked rubbers and the following standard expressions may be used for the free energies[25].

The free energy of dilution for a polymer solvent system ΔG_1 may be written as,

$$\Delta G_1 = RT\,[1n(1 - v) + v + \chi v^2] \qquad \text{...(3)}$$

where R is the universal gas constant, v the volume fraction of polymer, T the absolute temperature and χ the *Flory Huggins* interaction parameter. .

The change in elastic free energy on swelling is given by,

$$\Delta G_2 = (\rho RTVv^{1/3}) / M_c \qquad \text{...(4)}$$

where ρ is the density and v the molar volume of the swelling liquid. If we assume the solvent and chains are in equilibrium then

$$\Delta G_1 + \Delta G_2 = 0 \qquad \text{...(5)}$$

and

$$1n\,(1 - v) + v + \chi v^2 + (\rho Vv^{1/3}) / M_c = 0 \qquad \text{...(6)}$$

Therefore the equilibrium molecular weight between entanglements in the presence of solvents is given by,

$$M_c = -\,(\rho Vv^{1/3}) / (1n(1 - v) + v + \chi v^2) \qquad \text{...(7)}$$

Combining equation (2) and (6), yields

$$\lambda_{max} = \{(-\rho Vv^{1/3})\,[M_0\,\{1 - v) + v + \chi v^2\}]\}^{1/2} \qquad \text{...(8)}$$

In the experiments carried out only good solvents are used, which means that the *Flory Huggins* parameter, χ is small and can be ignored in relation to the other terms. In addition if v is significantly less than 1, the equation (8) can be approximated to,

$$\lambda_{max} = \{[2\rho Vv^{1/3}] / [M_0 (1-2\,\chi) v^2]\}^{1/2} \qquad \text{...(9)}$$

or, ignoring χ

$$\lambda_{max} = (2\rho V / M_o)^{1/2}\, v^{-0.83} \qquad \text{...(10)}$$

Equation (10) is similar to the *Smith*, *Lemstra* and *Booij* [26] equation with the exception of the value for the power law controlling the v dependence, which in the above derivation is - 0.83 rather than - 0.5. Logarithmic plots of λ_{max} as a function v are plotted for the experimental data in Figure 10. A least square fit to a straight line gives a best fit power law index of 0.861 for specimens drawn at 120°C which is in good agreement with equation (10). The good fit between the model and experimental results suggests that there is some justification in the initial assumption that the solvent and polymer are at, or near, equilibrium.

The success of the swell drawing process depends, among other variables, on the ability of a polymer to absorb large quantities of solvent without significant dissolution and loss of physical integrity and as such this process is not suitable for polymers with low molecular weight. This obserbation shows that the tensile drawing process may only be carried out on polymers with sufficiently high molecular weight. It is plausible that in the case of the lower molecular weight polymers, the average distance length of the molecular chains resulting in an excessive reduction of entanglements and loss of molecular connectedness.

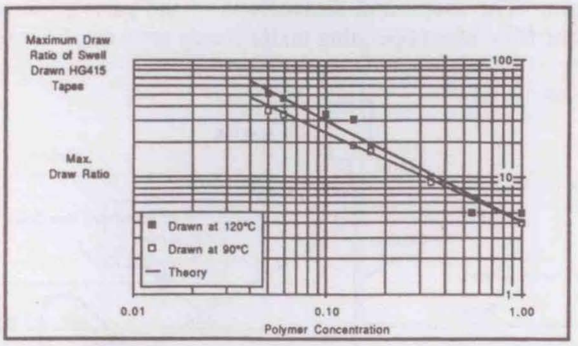


Figure 10 Theoretical fit of maximum draw ratio versus initial polymer concentration during swelling.

The swell drawing method offer a new route by which high melecular weight polyethylene can be processed in order to achieve high drawability and corresponding enhanced mechanical properties. In principle the process can be applied to polymers of any chosen geometry namely fibre or tape and in addition the swollen material can be biaxially drawn if desired. The process can readily be visualized as being continuous and one variant of a process line is shown schematically in Figure 11. A major potential advantage of this process is that the use of solvents is limited to a small region of the system and fluid processing of polymer gel is avoided.

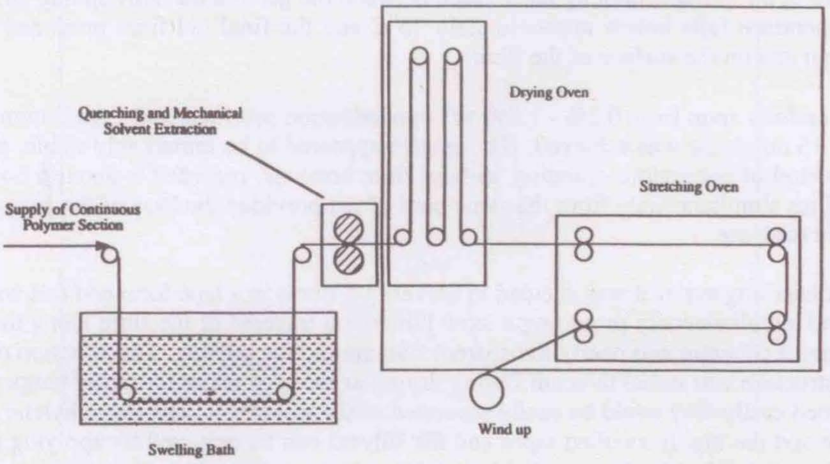


Figure 11 Schematic diagram of a swell drawing process.

The drawing behaviour of the swollen workpiece follows a similar pattern to the DSM [27] process in that the drawability increases with increased initial solvent loading. This behaviour appears to be quantitatively consistent with the above theoretical modelling which is based on the ultimate drawability of networks and equilibrium thermodynamics of solvent/polymer systems. Polymer crystallization certainly plays an important part in the drawing mechanism, however, the ultimate drawing behaviour of the material does appear to be controlled by the entanglement level of the longest chains within the solid polymer.

Die Free Gel Spinning

Another new technique which was developed by this author for producing high performance polyethylene fibres and tapes does not require the process fluid to pass through a die or spinneret[28]. In a gel state a polymer solution is capable of sustaining a reasonable tensile force. This unique property enables some polymer solution to be pulled away from the surface as observed in the *suspended syphon* phenomenon where it is possilbe to lift the intake of a syphon away from the fluid surface of a viscoelastic fluid without interrupting the syphoning process. The die free spinning process utilizes this phenomenon to produce a uniformly crystallized gel fibres which can then be oriented by the normal tensile drawing method.

The schematic arrangement of the die-free spinning process is shown in Figure 12. The arrangement consists of a quantity of gel kept in an open-topped beaker. The gel is maintained under quiescent conditions at the bulk temperature recorded within the fluid in the range T = 120 - 130^{0}C. Spinning is initiated by inserting a small metal rod of about 1.0 mm diameter into the solution and gently withdrawing the rod and attached gel fibre. The gel fibre was then threaded over a PTFE pulley and wound up on a motor driven spool. As the gel is withdrawn from the gel pool it forms a cylindrical parison which is stable and symmetric. Under typical drawing speeds of about 2 m/minute the base of the parison had a diameter of about 5 - 10 mm with a final diameter of order 1.0 mm. The shape and dimensions of the parison surprisingly appeared to be relatively independent of the windup up seed of the fibre when operating under steady state conditions.

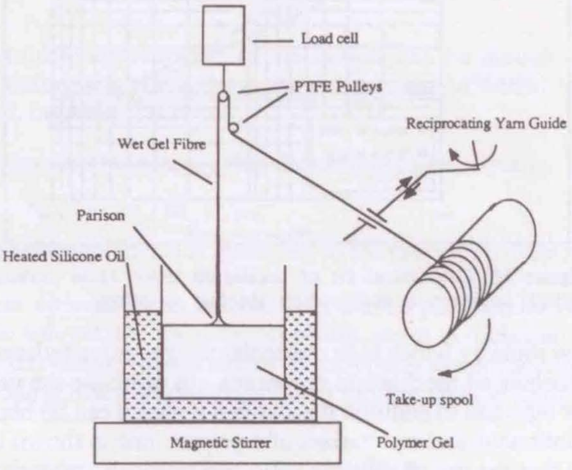


Figure 12 Schematic diagram of a die free spinning process.

When the gel fibre emerges at the surface, cooling takes place between the gel and the surrounding air. Crystallization of the gel begins when the temperature falls below approximately 75^{0}C and the final gel fibre produced is both compliant and contains solvent both within and on the surface of the fibre.

Gel fibres have been successfully spun from 0.2% - 1.0% w/v concentration solutions and a maximum spinning speed for the precursor wet gel fibre of 15 m/minute was achieved. The system appeared to be remarkably stable, giving a highly uniform fibre and the maximum period of continuous spinning without fibre breakage recorded is about 6 hours. In addition it was possible to spin several fibres simultaneously from the same pool of gel provided the base of the parison are kept sufficiently far apart so that they do not coalesce.

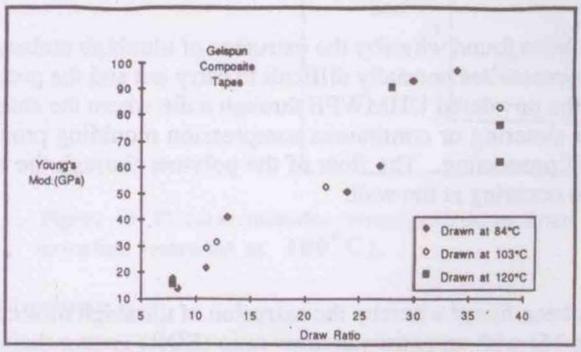
Partly to make subsequent handling easier it was decided to harvest gel fibres in a tape form and this was achieved by winding the fibre onto a bobbin and simultaneously providing a slow horizontal traverse of the fibre along the length of the bobbin. In this way the fibres formed a coherent and nearly transparent film around the bobbin. The adhesion of adjacent fibres which form the composite tape structure was noted to occur during drying at room or elevated drying temperature and even though the wet spun fibres soalesced easily they could be easily separated in the wet stage. The polyethylene film has charasteristics similar to that of a sponge and the highly swollen tapes and the solvent can be removed by applying mechanical pressure or by allowing evaporation to occur either for long periods at room temperaure or at elevated temperatures, but below the fibre melting point of about 138^{0}C. In most of the spinning experiments about 60% of the solvent used was recovered merely by placing a beaker under the take-up spool. The recovered solvent could be recycled without observable deterioration.

At this point the film has crystallinity with essentially no preferred molecular orientation. In order to achieve high chain anisotropy together with levels of high crystallinity the films were drawn at elevated temperature using a JJ^{TM} tensile testing machine in the range between 80 - 120^{0}C and at a crosshead speed of 100 mm/minute. The cross sectional area of the specimens was determined by weighing known lengths of the samples and assuming a bulk density of 1,000 kg/m^{3} for the polymer. It was found that draw ratios λ of between 1 - 50 could readily be achieved. The draw ratio being determined as the final increased length divided by the original length of grid spacings marked at 5mm intervals on the surface of the film.

Properties of die-free structures

The composite tapes were found to exhibit good drawability and excellent final mechanical properties. A *Youngs* modulus of 96 GPa was recorded for composite tape drawn to 34 times its original length at 84^{0}C as shown in Figure 13. These specimens were prepared from a 0.5% w/v solution spun at the rate of 2.0 metres/min. and the corresponding tensile strength was approximately 1.74 GPa for a specimen length of 150 mm.

The values of the tensile strength (Figure 14) are relatively low compared to the values reported for single strand fibres prepared by the gel extrusion process and the swell drawing technique reported above. This is attributed to the susceptibility of the composite tapes to fibrillate and fail at the grips. A draw ratio of up to 60 has been obtained for single strand fibres prepared under the above conditions. However it has not been possilbe to measure the mechanical properties of these single fibres using the facilities which existed.



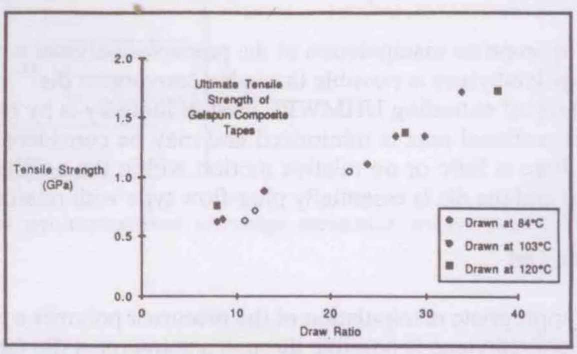


Figure 13 Young's modulus of gelspun composite tapes. Figure 14 Ultimate tensile strength of gelspun composite tape.

The DSC scans of the fibres drawn to 40X and carried out at a heating rate of 10 deg/min are shown in Figure 15 which indicated the presence of transitions at 149^{0}C and 159^{0}C. When these DSC traces of the die free spinning process are compared with those observed in the swell drawing experiments reported above two distinct differences are observed. The first is that for the same draw ratio the temperature of the endothermic peaks are higher for the swell drawn specimens than the gel spun fibres. The second difference relates to the development of the secondary and tertiary endothermic peaks. In the case of swell drawn specimens, the second peak begins to appear at a draw ratio of approximately 18 to 20 and the three distinctive peaks become very prominent at draw ratios $\lambda > 30$. For the same draw ratios $\lambda > 30$, only two peaks are observed in the gel spun fibres.

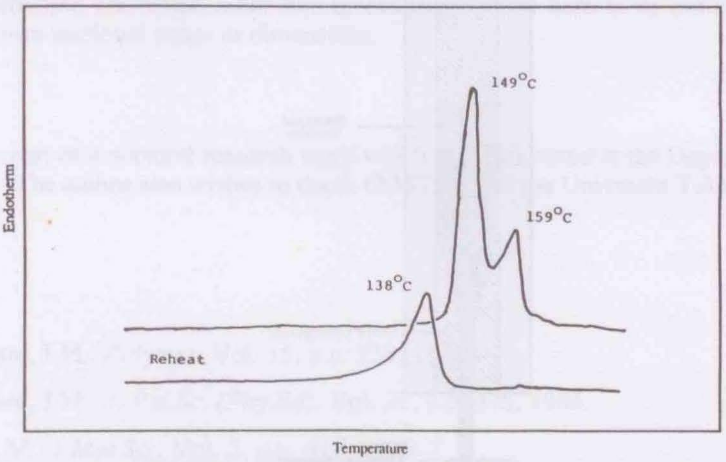


Figure 15 Differential scanning calorimeter traces of gelspun fibres. Draw ratio = 43 superimposed by the same specimen being reheated (same condition as Figure 8).

Discussion on die free spinning

The general findings of the die free spinning process are consistent with those of *Smith* and *Lemstra*[29] in that drawability of ultrahigh molecular weight polyethylene appears to be directly related to the low entanglement state produced by the processing from the gel state. Crystallization followed by elevated temperature drawing yields a high ratio and a very level of chain anisotropy with associated enhanced properties.

The die-free spinning has similarities to the rheological tubeless syphon experiment which amongst others has been investigated by *Macsporran*[30]. In this context the die-free spinning experiment does re present a pure extensional flow geometry which is worthy of detailed examination. It is not surprising to note that the precursor fibre was found to have essentially no anisotropy although it has been subjected to prior solidification in an extensional flow. The elongation rate was of the order 0.3s^{-1} was perhaps too low to cause any molecular orientation in the flowing polymer solution.

The die-free spinning process offers possible process advantabes over the spinneret route[31] in that amongst other factors, problems associated with melt flow instabilities[32], die swell and spinneret blockage are overcome. In addition the method of die free spining may also be a pplicable to systems that contain strong acids such as Lyotropic liquid crystal polyamide solutions where corrosion and wear of the spinneret is significant.

Extrusion Of Gel Crystallized UHMWPE

By the appropriate manipulation of the precursor polymer a route has been found whereby the extrusion of ultrahigh molecular weight polyethylene is possible through a convergent die[33]. Such processes are normally difficult to carry out and the present technology of extruding UHMWPE used in industry is by ramming the powdered UHMWPE through a die where the change in cross sectional area is minimized and may be considered to be a sintering or continuous compression moulding process where there is little or no relative motion within the polymer during processing. The flow of the polymer through the ram extruder and the die is essentially plug-flow type with relative motion occuring at the wall.

Experimental

By the appropriate manipulation of the precursor polymer a route has been found whereby the extrusion of ultrahigh molecular weight polyethylene is possible through a convergent die (see Figure 16) with an extrusion draw ratio (EDR) greater than 20. Where EDR is defined as the ratio of the cross sectional area of the extruder barrel to the final cross sectional area of the die exit. The basic steps of the process are;

i) Gel preparation
ii) Crystallization of gel
iii) Removal of solvent from the crystallized gel
iv) Development of anisotropy by extrusion
v) Determination of mechanical properties

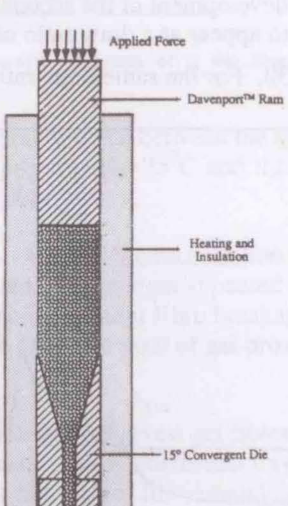


Figure 16 Schematic diagram of the ram extrusion of Gel crystallized ultrahigh molecular weight polyethylene.

Results

The flexural stiffness as measured in 3-point bending tests of the gel-crystallized extrudates are shown in Figure 17. There is clearly a monotonic increase of the mechanical properties of the extrudates with increasingly EDR indicating a progressive increase in molecular orientation in the specimen. Unfortunately for these specimens, it was difficult to obtain their mechanical properties in tension owing to the difficulty associated in gripping them in the testing machine.

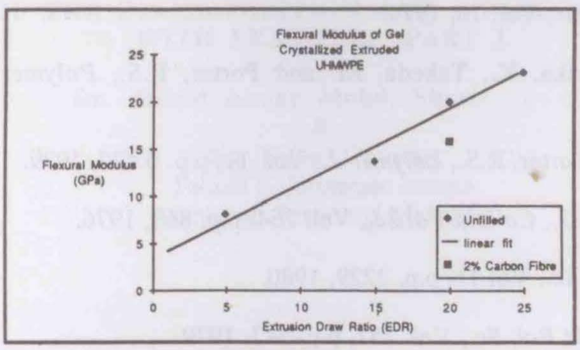


Figure 17 Flexural modulus versus extrusion draw ratio of gel crystallized ultrahigh molecular weight polyethylene extrudate (extruded at 100^0 C).

Conclusions

The development of high performance thermoplastics such as high performance polyethylene (HPPE) has been shown to be made possible by the availability of the ultrahigh molecular weight grades ($M_W > 10^6$ kg/kmol). Unfortunately these grades have proved to be difficult to process owing to its high intrinsic viscosity and the consequent high levels of molecular entanglements has been shown to be possible by crystallazation from solution as demonstrated by the gel spining processes or by crystallization from a swollen state as demonstrated by the swell-drawing process.

Of the three new processes for the manufacture of HPPE reported here, the die-free spinning process is an extremely simple process for the preparation of gel fibres for subsequent treatment to produce a strong stiff structure. Its simplicity implies that such experiments may be conducted in even the most basic laboratory for demonstration or research purposes. A similar arguent may also be used for the swell-drawing process. In addition the greatest advantage of the swell-drawing process is the limited involvement of the solvent where it is confined to only the swelling stage of the process. Finally the main advantage of the gel-crystallized extrusion above the other two methods proposed here is its ability to produce monolithic HPPE structures to almost any cross-sectional shape or dimensions.

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