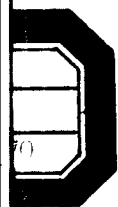


70 Advances in Polymer Science

Key Polymers Properties and Performance

With Contributions by

R. M. Aseeva, M. Biswas, S. Packirisamy,
S. Rostami, D. J. Walsh, I. M. Ward,
G. E. Zaikov



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With 117 Figures and 22 Tables



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Editorial

With the publication of Vol. 51 the editors and the publisher would like to take this opportunity to thank authors and readers for their collaboration and their efforts to meet the scientific requirements of this series. We appreciate the concern of our authors for the progress of "Advances in Polymer Science" and we also welcome the advice and critical comments of our readers.

With the publication of Vol. 51 we would also like to refer to a editorial policy: *this series publishes invited, critical review articles of new developments in all areas of polymer science in English (authors may naturally also include works of their own)*. The responsible editor, that means the editor who has invited the author, discusses the scope of the review with the author on the basis of a tentative outline which the author is asked to provide. The author and editor are responsible for the scientific quality of the contribution.

Manuscripts must be submitted in content, language, and form satisfactory to Springer-Verlag. Figures and formulas should be reproducible. To meet the convenience of our readers, the publisher will include "volume index" which characterizes the content of the volume.

The editors and the publisher will make all efforts to publish the manuscripts as rapidly as possible, i.e., at the maximum six months after the submission of an accepted paper. Contributions from diverse areas of polymer science must occasionally be united in one volume. In such cases a "volume index" cannot meet all expectations, but will nevertheless provide more information than a mere volume number.

Starting with Vol. 51, each volume will contain a subject index.

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Publisher

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The Preparation, Structure and Properties of Ultra-High Modulus Flexible Polymers

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In this review the preparation, structure and properties of ultra-high modulus polyolefins are discussed. First, detailed consideration is given to the preparation of ultra-high modulus polyethylene and polypropylene fibres by spinning from dilute solution and by gel-spinning and hot drawing. This is followed by an account of the tensile drawing procedures which have led to the production of high modulus fibres and films in polyethylene, polypropylene and polyoxymethylene. Finally, consideration is given in the production of high modulus solid section products (rod, sheet and tube) in all these polymers by ram extrusion, hydrostatic extrusion and die-drawing.

It is concluded that in these different processing routes the overriding consideration is to achieve very high extensional deformation at a molecular level. The structure of the initial isotropic polymer is therefore of key importance, the essential requirement being an adequate but not restrictive number of molecular entanglements, so that the molecular network can be stretched effectively to very high draw ratios and give very high molecular orientation. Molecular weight and morphology are therefore important, together with the drawing conditions which must permit sufficient mobility for the chains to move freely between network entanglements.

Following a review of present structural understanding of these highly oriented polymers, a detailed account is presented of mechanical behaviour, including dynamic mechanical relaxations, creep and strength. This is followed by discussion of thermal properties (melting behaviour, thermal conductivity, thermal expansion, shrinkage) and barrier properties (permeability to liquids and gases, solubility). It is of some practical importance that the improvements in stiffness and strength are accompanied by substantial improvements in thermal stability, in barrier properties and in chemical resistance.

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List of Symbols

B	Constant
c	Surface crack length
\bar{c}	Fitted constant
d	Fibre diameter
d_r	Die exit diameter
E	Young's modulus
E_c	Crystal modulus
E_m	Modulus of Maxwell element
E_v	Modulus of Voigt element
G_c	Strain energy release rate
k	Boltzmann's constant
$K_{ }$	Thermal conductivity parallel to orientation direction
K_{\perp}	Thermal conductivity perpendicular to orientation direction
L	Long period
\bar{L}_{002}	Average crystal thickness
m	Constant
m_s	Molecular weight of a statistical segment
M_e	Molecular weight between entanglements
\bar{M}_n	Number average molecular weight
\bar{M}_w	Weight average molecular weight
N_c	Number of statistical chain segments between crosslinks
N_e	Number of statistical chain segments between entanglements
p	Probability of crystalline sequence linking two adjacent lamellae
P	Hydrostatic pressure
S	Amorphous phase solubility
R	Deformation ratio at distance x from die cone apex
R_A	Actual deformation ratio
R_N	Nominal deformation ratio
t	Time
T	Absolute temperature
ΔU	Activation energy
v	Shear activation volume
v_r	Die exit velocity
x	Distance from die cone apex
Y	Geometric factor
α	Die semi-angle
α_0	Intrinsic thermal expansivity
$\alpha_{ }$	Thermal expansivity parallel to orientation direction
ϵ	Strain
$\dot{\epsilon}$	Strain rate
$\dot{\epsilon}_0$	Pre-exponential factor
$\dot{\epsilon}_p$	Plateau creep rate
ϵ/k	Lennard-Jones force constant
λ	Draw ratio

λ_{\max}	Maximum draw ratio
Φ	Polymer volume fraction
σ	Stress
σ_B	Breaking stress
σ_0	Applied stress
σ_T	Tensile stress
τ	Retardation time of Voigt element
τ_f	Shear flow stress
Ω	Pressure activation volume
η_m	Viscosity of Maxwell element
η_v	Viscosity of Voigt element

1 Introduction

Although it had been appreciated since the early studies of Meyer and Lotmar¹⁾ in the 1930's that there was a substantial gap between the theoretical stiffness of the chain in several commercially available polymers and the achievement of stiffness by existing processes, it was not until the 1970's that this gap was bridged. It is in polyethylene that the results have been most dramatically realised, and oriented fibres and rods have been produced with room temperature Young's moduli in the range from 50–100 GPa^{2–7)}. Solution spun fibres have even been prepared with a Young's modulus at low temperatures of 288 GPa⁸⁾, which is very close to the highest theoretical estimate of 324 GPa⁹⁾.

In this review article, an account will be presented of the different methods by which high modulus materials have been produced from flexible polymers. Much of the discussion will be concerned with polyethylene, although comparable results have been obtained for polypropylene and polyoxymethylene, and these will also be considered. The initial stimulus to this research came from the quest for high stiffness, but other properties have also been enhanced, including strength, thermal and chemical stability, and barrier properties. The present article updates and extends previous reviews^{10–12)} of progress in this exciting new area of polymer science.

2 Solution and Melt Processes

2.1 Solution Spinning and Drawing

A remarkable development in polymer science was the observation by A. J. Penning^{13–15)} that, when dilute solutions of polyethylene were cooled under conditions of continuous stirring, very fine fibres were precipitated on the stirrer. These fibres possessed a remarkable morphology consisting of a fine central core of extended chain polyethylene with an outer sheath of folded chain polymer material, so that electron microscopy revealed a beautiful shish-kebab structure. The possible significance of this result was recognised by Frank¹⁶⁾, who emphasised the importance of extensional as distinct from shear deformation in achieving high molecular extension and hence high modulus. This idea was developed in elegant series of experiments by Frank, Keller, Mackley^{17–24)} and their colleagues at Bristol University where converging jets or rollers were used to create elongational flow fields in both flowing solutions and melts. It did not prove possible, however, to produce high modulus material. In the case of the solutions the proportion of central core extended chain material to outer sheath chain-folded material was comparatively low. In melts, it appeared that if the conditions were chosen to reduce the rate of chain-folded crystallisation the overall rate of solidification became so fast that flow ceased.

A further breakthrough in this area was then achieved by Zwiijnenberg and Penning⁶⁾ in 1976, with the discovery that ultra high modulus polyethylene fibres could be produced by "seeded crystallisation" of fine fibres, winding up at very high temperatures. In the optimum arrangements for this process shown in the schematic diagram

of Fig. 1, the seed crystal is located between the inner and outer surface of a Couette viscometer. With the seed crystal in the middle of the gap "free growth" was obtained similar to that observed previously by Zwijnenberg and Pennings²⁵⁾ under laminar flow conditions. When the seed crystal comes into contact with the rotor surface, the so-called 'surface growth' occurs where continuous production of a very fine fibre can be maintained for several days. Moreover, by growing fibres at high temperature, materials with truly remarkable properties were obtained. A set of stress-strain curves is shown in Fig. 2, from which it can be seen that a modulus of ~ 100 GPa and a tensile strength of 3.5 GPa can be achieved. Detailed studies by Pennings and his collaborators²⁶⁾, and by Keller and his collaborators^{24, 27)} have shown that the formation of a very high molecular weight gel layer by absorption on the rotor surface plays a vital role. The molecular network of the gel layer is then stretched in the elongational flow field to give the high modulus product. The limitation of this approach is the comparatively low production rate, which was about 150 cm/min, limited by fibre fracture at the highest haul-off rates.

The next major development takes up the idea of the gel layer, and combines this with the tensile drawing of fibres at high temperature, hopefully to give a preparation route which is more acceptable in terms of production rates. We therefore now have a two stage process, in which a fibre of suitable initial structure is first produced, followed by a hot stretching process, and historically two parallel accounts have been given more or less contemporaneously. Smith and Lemstra⁷⁾ describe the

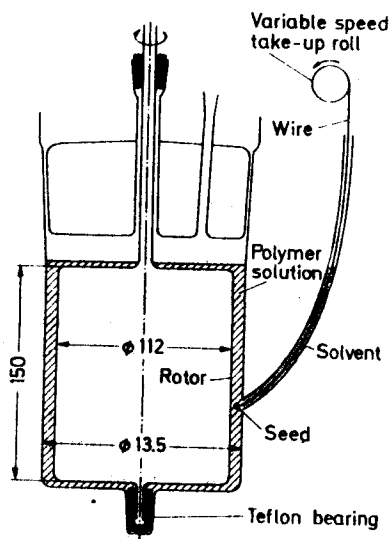


Fig. 1

Fig. 1. Couette apparatus (A) for continuous growth of polyethylene macrofibres from dilute p-xylene solutions. The macrofibre grows on the surface of the Teflon rotor, leaves the vessel through a Teflon pipe, and is wound up on a take-up roll.

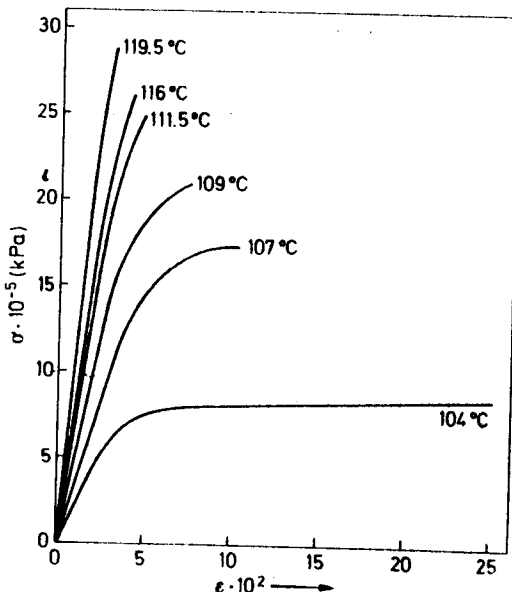


Fig. 2

Fig. 2. Stress (σ)-strain (ϵ) curves for some polyethylene macrofibres grown from a 0.5% xylene solution by the surface growth technique at various temperatures

production of a gel fibre by spinning a 2% solution of high molecular weight polyethylene in decalin into cold water. The gel fibre is dried and then drawn in a hot air oven at 120 °C. At the highest draw ratio ~ 30 , a fibre with 90 GPa modulus and 3 GPa tensile strength was obtained. Kalb and Pennings²⁸⁾ describe the production of a "porous" fibre by spinning a 5% solution of polyethylene in paraffin oil. Again the fibre is dried, and in this case drawn in a temperature gradient from 100–148 °C to a draw ratio of 16. This gave a product with 106 GPa modulus and 3 GPa tensile strength.

The preparation of polyethylene fibres with strengths in the range 3–4 GPa by the gel spinning route described by Pennings as discussed above, required spinning extrusion speeds of about 1 m/min. Although higher spinning speeds could be achieved by stretching the filaments in the molten state, this led to a dramatic reduction in the final strengths after drawing. For example a strength of less than 0.5 GPa was obtained for a winding up speed of 20 m/min. Pennings and his colleagues²⁹⁾ have speculated that this relates to recoiling of the molecules leading to the generation of elastic turbulences which then disrupt the entanglement network so that the molecules are not elongated in the drawing process. Smook and Pennings³⁰⁾ have shown that the addition of 1% (weight) of Aluminium stearate ($\text{Al}(\text{OOC}_{17}\text{C}_{35})_3$) permits the tensile properties after drawing to be retained to comparatively high wind up speeds (Fig. 3). It has been proposed that an absorbed aluminium stearate layer will be formed between the flowing polymer solution and the die wall. This layer then inhibits the occurrence of elastic flow instabilities. The effectiveness of adding aluminium stearate is limited to low concentrations. At higher concentrations, the aluminium stearate provides the formation of more intramolecular entanglements which are not effective in stretching the molecules.

Pennings and his collaborators²⁹⁾ have examined the hot drawing behaviour of the range of spun fibres. The fibres were stretched between moving rollers, and the draw ratio determined as the ratio of the take-up speed on the second roller to the

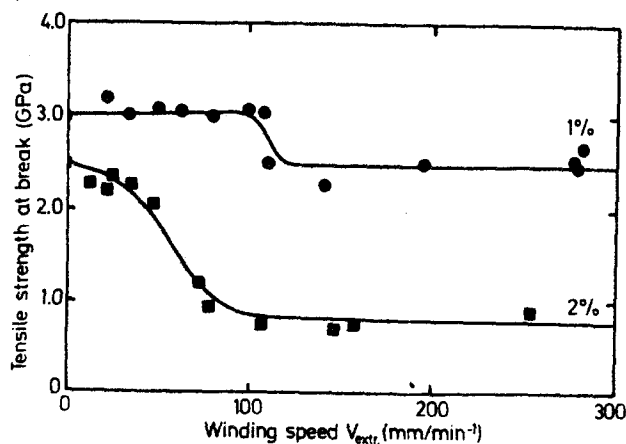


Fig. 3. Tensile strength at break, σ_b , after hot-drawing against take-up speed during gel-spinning of UHMWPE at different concentrations of aluminium stearate (wt.-%) in the spinning solution (Die: $c = 14.5$ cm, $\alpha = 6^\circ$ and $D = 1.8$ mm). With permission of the publishers Chapman & Hall Ltd, (C)

input speed on the first roller, which corresponded to a constant velocity of 2.65 cm/min. The importance of a parallel oriented shish kebab morphology at the spinning stage, as well as the topology of the entanglement network, has been emphasised. Smook³¹⁾ has envisaged the hot drawing process as involving the deformation of a structure consisting of alternating bundles of elongated molecules and clusters of unoriented molecules, which are connected to each other by entanglement couplings. Pennings and his collaborators^{29, 31, 32)} have measured the axial tensile force as a function of time for stretching the fibres from a draw ratio of 3.5 to the maximum draw ratio over a wide temperature range. The results were analysed on the basis that stress is generated overcoming viscous flow. An apparent elongational viscosity is then derived as a function of temperature and draw ratio. It is suggested that there are three distinct temperature regions identified by different activation energies. There is a low temperature regime associated with the flow of separate fibrils and the unfolding of lamellar crystals, an intermediate regime where the lamellae melt and the fibrils aggregate, and a high temperature regime of very high chain mobility where slippage of individual chains occur. Although these speculations are attractive, it is clear that there is still room for a more comprehensive phenomenological treatment.

Some further studies of the gel spinning and drawing process have been undertaken by Manley and co-workers³³⁻³⁵⁾. In polyethylene, their efforts were concentrated on two aspects. First, there was the drawing of dried gel films at ambient temperatures. These gel films had a structure similar to single crystal mats where the lamellar crystals are oriented parallel to the film surface. Draw ratios of 20 could be obtained, much greater than for cold drawing of high molecular weight bulk polymer. Moreover, by annealing these gel films at 110 °C, the maximum draw ratio could be increased to 30. This improvement was attributed to the increase in entanglements to act as inter-lamellar crosslinks and give more effective drawing.

In a further development Peguy and Manley³⁶⁾ report the drawing of polypropylene gel films. The key result is summarised in Fig. 4, which shows the modulus/draw ratio

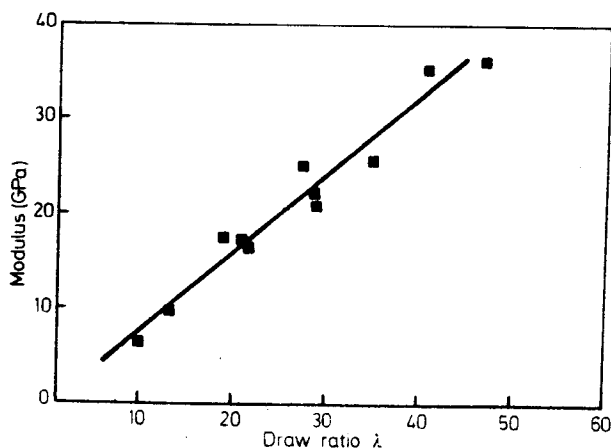


Fig. 4. Young's modulus/draw ratio relationship for dry polypropylene gel films at 140 °C. With permission of the publishers Butterworth & Co. (Publishers) Ltd. (C)

relationship for drawing at 140 °C. It is remarkable to note that values of draw ratio as high as 57 were recorded, and modulus results were obtained for draw ratio 47.5, where a value of 36 GPa was obtained. This is very close to the theoretical estimates and crystal strain values of ~40–45 GPa.

2.2 Molecular Entanglements and the Stretching of a Molecular Network

In the one-stage solution surface-growth technique as well as the two-stage gel spinning and drawing route, it has been established that the absorption of the very high molecular weight polyethylene on the rotor surface and the formation of a gel layer are key features. In the original method of Pennings and his co-workers the entanglement network of the gel is stretched in the elongational flow field of a Couette or Poiseuille flow apparatus, as originally postulated by Frank¹⁶⁾, and clearly illustrated in subsequent experiments by Frank, Keller and Mackley^{17–23)}.

It can therefore be concluded that the production of high modulus polyethylene occurs by the stretching of a molecular network in the solid phase deformation routes of tensile drawing, hydrostatic and ram extrusion and die drawing, and for the solution routes of one-stage surface growth and gel spinning and drawing. In all cases the limiting draw ratio λ_{\max} relates to the chain length between entanglements.

For a simple rubber-like network, the maximum draw ratio varies with the number N_e of statistical chain segments between crosslinks as

$$\lambda_{\max} = (N_e)^{1/2} \quad (1)$$

In the solid phase, support for a similar contention has come from the drawing of polyethylene terephthalate, combined with stress optical measurements, and also for the behaviour of craze fibrils in a range of glassy polymers.

Smith, Lemstra and Booij³⁷⁾ developed a similar argument for a gel-spun fibre. The molecular weight between entanglements in the undiluted polymer melt is denoted by M_e . The number of statistical chain segments between entanglements is given by

$$N_e = \frac{M_e}{m_s},$$

where m_s is the molecular weight of a statistical chain segment. In a solution with a polymer concentration c exceeding the value for onset of coil-overlap, the molecular weight between entanglements $(M_e)_{\text{soln}}$ is greater and is given approximately by

$$(M_e)_{\text{soln}} = (\rho/c)M_e = M_e/\Phi \quad (2)$$

where ρ is the bulk density of the polymer and Φ is the polymer volume fraction.

Smith et al. assume that the entanglements are equivalent to crosslinks, so that $N_e = N_c$.

Combining equations (1) and (2) then gives

$$\lambda_{\max \text{ gel}} = (N_e)_{\text{soln}}^{1/2} = (N_e/\Phi)^{1/2} = \lambda_{\max \text{ solid}}\Phi^{-1/2} \quad (3)$$

where $\lambda_{\max \text{ gel}}$ and $\lambda_{\max \text{ solid}}$ are the limiting draw ratios for the gel spun and drawn and solid phase drawn polymers respectively.

M_e for high molecular weight PE is reported by Smith et al. as 1900, giving $N_e = 13.6$ and $\lambda_{\max \text{ solid}} = 3.7$.

The results obtained by drawing gel spun polyethylene fibres at different temperatures are shown in Fig. 5. It can be seen that the relationship between $\lambda_{\max \text{ gel}}$ and $\Phi^{-1/2}$ predicted by Eq. (3) holds to a good approximation. Furthermore, the intercept at $\Phi = 1$ for a draw temperature of 90 °C was found to be 3.8, in good agreement with the value of 3.7 estimated above. The higher values of $\lambda_{\max \text{ gel}}$ at higher temperatures were attributed to chain slippage.

Pennings and his colleagues²⁹⁾ have remarked on the influence of the hot drawing process in reducing the number of entanglements from that existing in a quiescent solution. For example, for a 5% solution of polyethylene in paraffin oil, with $\Phi \approx 0.6$, a value for $M_e (\text{soln})$ of 17×10^3 kg/kmol can be estimated, corresponding to about 12 entanglements per chain. By subjecting fibres to a series of cross-linking treatments by irradiation, it was possible to determine the number of effective network chains in the gel for each irradiation treatment on the basis of swelling measurements. Extrapolation to zero radiation dose then gave a value of 2 entanglements per chain in the unirradiated drawn fibre, a marked reduction from the value of 12 for the solution.

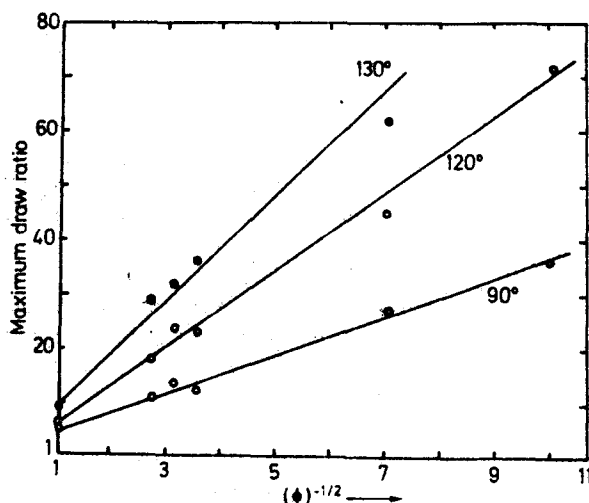


Fig. 5. Maximum draw ratio vs (initial polymer volume fraction)^{-1/2} at the indicated temperatures. With permission of the publishers John Wiley & Sons, Inc. (C).

2.3 Crystallisation During Melt Flow Under Pressure

High modulus polyethylenes have also been produced by the application of pressure to the polymer when it is molten under conditions of extrusion through a narrow capillary. It appears that in one case at least these methods differ in kind from those which involve stretching the molecules either in solution, or in the solid phase.

Van der Vegt and Smit³⁸⁾ observed that blockage could occur when molten polyethylene is extruded in a capillary rheometer under conditions where the polymer would be expected to remain fluid. This observation was followed up by Southern and Porter^{39,40)}, who examined the effect of a sudden minor reduction in temperature (by 1 °C say) during the extrusion of polyethylene in an Instron rheometer. It appeared that the large increase in pressure which occurred was due to crystallisation in the elongational flow field, which leads to termination of flow. A transparent strand of polyethylene could be extracted from the capillary. This varied in properties across its section and the overall dynamic modulus of 6.6 GPa, measured at 110 Hz, was comparatively low⁴¹⁾. However DSC measurements indicated a high melting component which was attributed to extended chain material, and later research described the measurement of moduli of a higher order of magnitude. In subsequent work by Porter and his colleagues⁴²⁾, the pressure was maintained so that the plug of solid crystallised polymer was slowly extruded. Later studies by this group have moved to straight extrusion of a pre-formed billet. This is akin to ram-extrusion and hydrostatic extrusion and is discussed elsewhere in this review.

Southern and Porter's original studies were extended in a more precise fashion by Keller and co-workers⁴³⁾ in a series of experiments where the flow of polymer in the capillary rheometer was deliberately stopped by sudden insertion of a needle valve. This produced a sudden rise in pressure, and crystallisation of the polymer. After cooling to room temperature, the plug of polymer was removed and was found to possess a very high modulus of ~70 GPa. Its structure was however quite different from other high modulus polyethylenes. A clear SAXS pattern was observed corresponding to a lamellar texture with a long period of ~300 Å. The comparatively low melting point showed that there was no extended chain material present. On the contrary, transmission electron microscopy revealed a structure of interlocking penetrating lamellae. It was suggested that the high modulus is due to the constraints on the rubber-like material between the lamellae, similar to that observed when sheets of steel are laminated with thin layers of rubber. Due to the incompressibility of the rubber and the lateral constraints imposed by bonding to the steel plates, the axial deformation of the rubber is severely restricted.

3 Solid Phase Deformation Processes

3.1 Tensile Drawing

The developments in high draw polyethylene stemmed initially from an exploratory examination by Andrews and Ward⁴⁴⁾ of the influence of molecular weight and molecular weight distribution on the drawing of linear polyethylene at ambient temperatures. In spite of considerable scatter in the results, due primarily to difficulties in controlling polymer morphology in the small scale spinning and drawing experiments, it was concluded that the draw ratio was sensitive to \bar{M}_w , the weight average molecular weight. A second important observation was the excellent correlation between the modulus of the drawn fibres and the draw ratio, the modulus increasing from 4 to 20 GPa as the draw ratio was increased from 7 to 13.