Swell drawing: A new method of manufacturing high performance polyethylene structures

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We report a new method for obtaining high strength, high stiffness polyethylene structures. Starting from a tape of ultrahigh molecular weight polyethylene we have found conditions under which the tape can be significantly swollen by a solvent whilst preventing any dissolution. The swollen polymer tape is then cooled to allow crystallization to occur and it is subsequently hot drawn. By this method we are able to achieve draw ratios in excess of 30× with a resulting Youngs modulus in excess of 100 GPa. We present in the paper experimental data on the swelling and drawing behaviour of this system together with a model that attempts to explain the enhanced drawability of swollen samples.

(Keywords: polyethylene; high modulus; high performance; fibres; tapes; swelling)

INTRODUCTION

The achievement of high mechanical stiffness and strength from flexible and linear commodity polymers has received extensive investigation over the last ten years. Notably work pioneered by Ward *et al.*[1] has led to solid state forming processes where in particular, enhanced stiffness has been achieved. In addition to the pioneering studies of Zwijnenburg and Pennings[2], Smith *et al.*[3,4] discovered the gel processing route for the manufacture of high stiffness and strength ultrahigh molecular weight polyethylene fibres. The route of Smith and Lemstra[4] requires the polymer to be dissolved in a solvent, extruded, quenched and then subsequently hot drawn. Smith and Lemstra claimed that the enhanced drawability of the gel fibre is a direct consequence of the reduction in polymer entanglement density in the precursor gel.

We have discovered conditions under which high drawability can be achieved without resorting to dissolution or fluid processing. The technique relies on starting with a workpiece of 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.

Rather surprisingly we have found little information in the literature relating to the simultaneous kinetics of swelling and dissolution in polymers. In general the literature divides into three areas namely swelling behaviour of crosslinked systems[5,6], the dissolution of polymers[7] and the diffusion of solvents into amorphous polymers[8-10]. Each of these areas are related to the effect we are observing, however it would appear that other workers have not previously operated in the regime where for uncrosslinked systems, significant swelling can occur without dissolution. This is probably due to the fact that we have been examining ultrahigh molecular weight polymer where the initial entanglement concentration is high and the reptation times of some chains are long.

METHOD

The sequence for our 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 (i) and (ii) can be combined and steps (iv) and (v) fully or partially interchanged.

(i) Manufacture of precursor workpiece

For our initial experiments we have chosen to use a tape geometry where the typical thickness of the tape is 0.3 mm and width 5 mm. The processing of tapes to this thickness usually presents little difficulty and for the lower molecular weight polyethylenes we were able to prepare continuous lengths of tapes using a conventional 18 mm Betol single screw extruder and slit die. As the molecular weight of the polymer increases, conventional screw extrusion technology becomes more difficult and ultrahigh molecular weight polyethylene (UHMWPE) with an M_n and M_w greater than 10^6 cannot be processed by this means. We were however able to obtain 0.3 mm thickness tapes from Performance Plastics Ltd. (Bacup, UK). These tapes had been skived from a block of UHMWPE which in turn had been manufactured by a continuous ram extrusion/sintering process. In all cases the starting tapes were visually defect free, with a smooth surface finish and were without any preferred molecular orientation.

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(ii) Swelling

We have examined the solvent uptake behaviour of three different molecular weight grades of polyethylene in xylene ($C_6H_4(CH_3)_2$) and one grade of polyethylene in dekalin ($C_{10}H_{18}$). In this paper the initial sample geometry was kept constant and we report observations only on 0.3 mm thickness samples.

The swelling and solvent uptake measurements were carried out by immersing a weighed piece of tape suspended on a fine resistance wire into a container of heated solvent for a given period. The swollen tape was then removed from the fluid and transferred onto a microbalance which was connected to a chart recorder. The weight of the swollen polymer was observed to decrease with time, initially at a fast rate, due to the solvent percolating out of the spongy structure of the swollen polymer and then at a slower rate as solvent loss by evaporation predominates. The total weight of the swollen polymer ($W_s + W_p$) was obtained by extrapolating the weight-time curve to the instant the polymer was removed from the solvent. Solvent evaporation was allowed to continue and the 'dry' sample weight was taken in order to ensure there was negligible polymer weight loss ($<5\%$) from the sample. The swelling results reported in this paper are reproducible and accurate to an estimated value of 10%. Significant scatter develops when dissolution starts to occur.

The results of the solvent uptake experiments are shown in *Figures 1–4* where ratios of the solvent weight, W_s to polymer weight W_p are plotted as a function of immersion time. *Figures 1–3* show the solvent uptake of xylene for progressively higher molecular weight grades of linear polyethylene. *Figure 1* shows the curves for Rigidex type 006-60 ($M_w = 135\,000$ and $M_n = 25\,500$) at three immersion temperatures 100°C, 105°C and 110°C. The curves show a steady increase in solvent uptake with time and as expected the rate of uptake increases with increasing temperature. For the 006-60 material when W_s/W_p approaches about 2, some dissolution, recorded as a dry weight loss is observed which in turn leads to an increasing scatter of the data. The geometrical and mechanical integrity of the material was essentially lost when W_s/W_p exceeded about 3.

As shown in *Figure 2*, by using a higher molecular weight grade Rigidex H060-45P ($M_w = 283\,000$ $M_n = 23\,000$) we were able to obtain an increase in the maximum value of W_s/W_p to $\sim$6–7 by immersion at 100°C. This set of results showed a curious trend in that increasing the temperature tended to decrease the value of W_s/W_p for a given immersion time. The solvent uptake for UHMWPE Hostalen GUR 415 (M_n and $M_w > 10^6$) is shown in *Figure 3*. These curves show that for an immersion temperature of 110°C it is possible to achieve a W_s/W_p ratio up to about 10. *Figure 4* shows curves for the

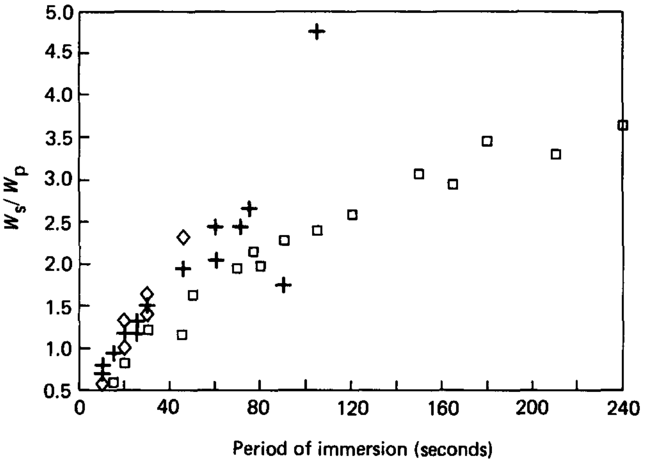

Figure 1 Solvent uptake curves for 006-60 tapes, 0.3 mm thick in xylene; (□) 100°C, (+) 105°C, (◇) 110°C

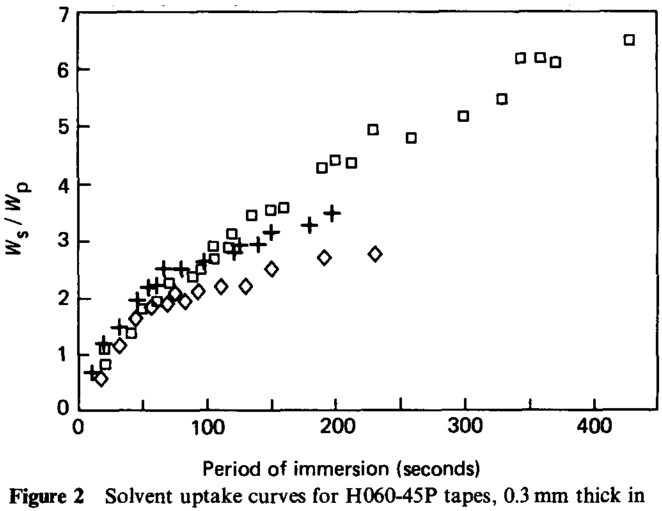

Figure 2 Solvent uptake curves for H060-45P tapes, 0.3 mm thick in xylene; (□) 100°C, (+) 105°C, (◇) 110°C

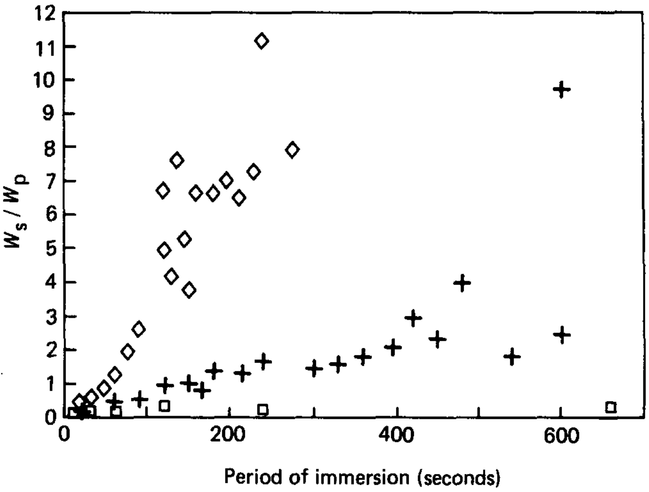

Figure 3 Solvent uptake curves for Hostalen GUR 415 tapes, 0.3 mm thick in xylene; (□) 100°C, (+) 105°C, (◇) 110°C

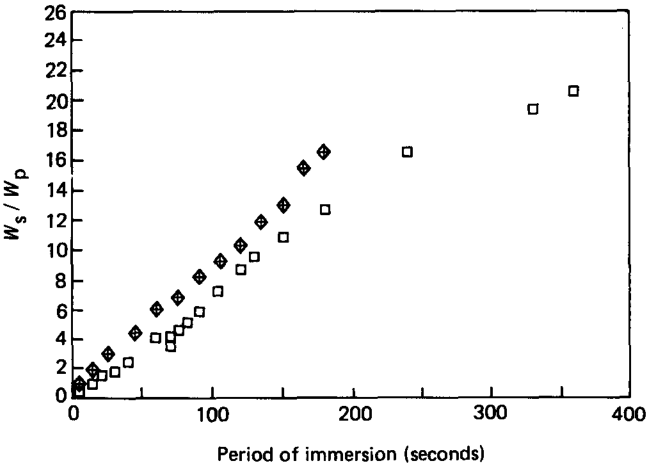

Figure 4 Solvent uptake curves for Hostalen GUR 415 tapes, 0.3 mm thick in dekalin; (□) 120°C, (◈) 130°C

same polymer but in this case using dekalin as a solvent. The curves show that W_s/W_p ratios for this system can exceed 20. Dekalin is a somewhat 'poorer' solvent than xylene, however its higher boiling point enables swelling experiments to be carried out at temperatures greater than the xylene system.

Visually the ingress of solvent into the polymer appears to follow case II diffusion in that a sharp solvent front is observed to penetrate into the material from the surface. In *Figure 5a* the early penetration of dekalin into Hostalen GUR is shown from a scanning electron micrograph of a fractured surface. Solvent penetration is observed as a coarse porous texture when compared to the smooth unswollen surface. In the case shown in *Figure 5a* after about 10 s at 130°C the solvent has penetrated 10–15 % of the starting thickness. Under these conditions the solvent fronts meet after about 20–30 s. *Figure 5b* shows the solvent ingress for dekalin into 006-60. For this example, after 40 s at 100°C the solvent has penetrated roughly 30% of the starting thickness from each face and under these conditions the solvent fronts meet after approximately one minute. The corresponding solvent uptake curve shown in *Figure 4* does not however indicate the classic case II behaviour where uptake proceeds linearly with time until the fronts meet and then saturates to a constant value. In our case solvent uptake proceeds well beyond the point in time when the solvent fronts meet.

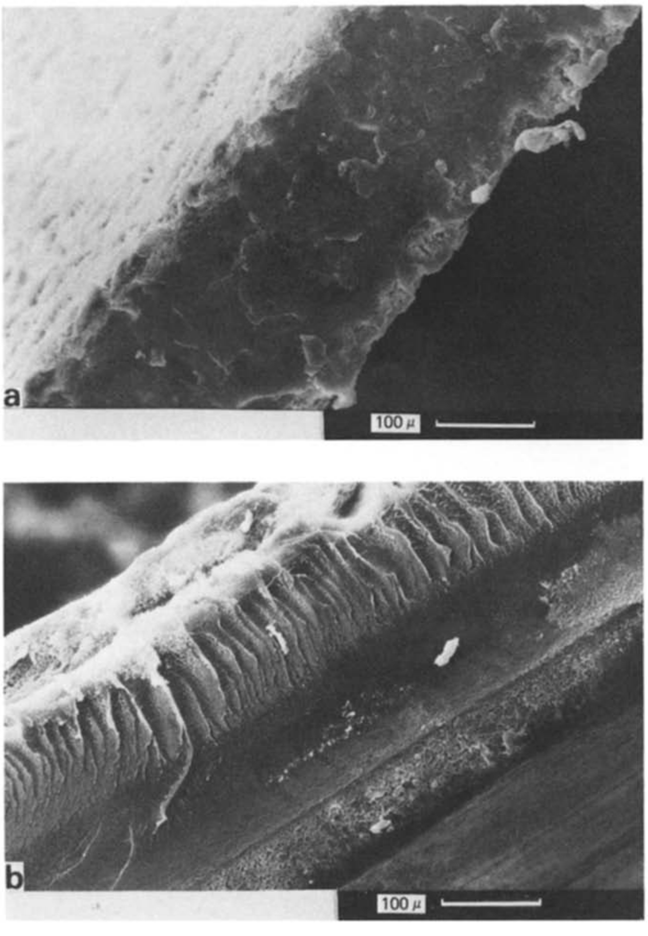

Figure 5 Scanning electron micrographs of fracture surface of partially swollen tapes in dekalin showing the presence of distinct swelling fronts; (a) Hostalen GUR tape immersed at 130°C for 10 s; (b) 006-60 tape immersed at 100°C for 40 s

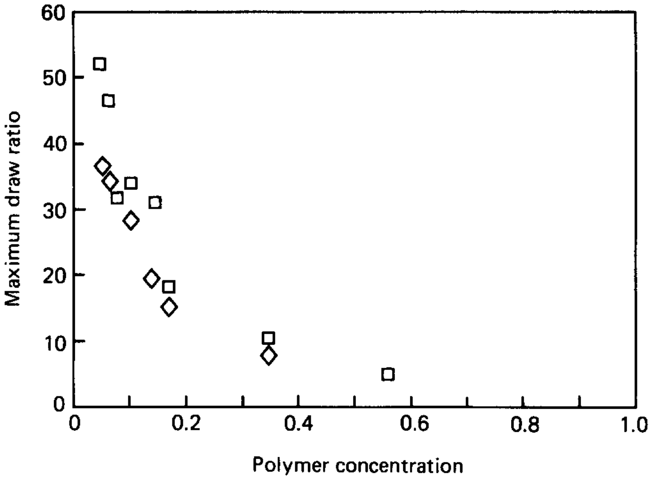

Figure 6 Maximum draw ratio *versus* initial solvent concentration for swell drawn Hostalen GUR tapes; (□) draw temperature = 120°C, (◇) draw temperature = 90°C

(iii) Quenching, crystallization and (iv) Solvent removal

At the swelling temperature and in the swollen state the tapes could be drawn but deformation was dominantly of a viscous nature and consequently little or no anisotropy developed with drawing. In order to ensure molecular orientation, the samples were cooled to room temperature in order to allow crystallization of the swollen workpiece to occur. No particular precautions were taken to slow or rapidly quench the samples and they were simply removed from the solvent bath and allowed to cool under ambient conditions.

Solvent removal from the workpiece was carried out by placing the workpiece in a JJ environmental cabinet at 80°C. It was however noted that at this stage the workpiece had the characteristics of a porous wet sponge and much of the solvent could be removed from the sample at room temperature by merely applying mechanical pressure to the tape thereby squeezing the solvent out from the polymer.

(v) Development of anisotropy by drawing

Molecular orientation was induced into the sample by means of mechanical drawing in a JJ tensile testing machine fitted with an environmental heating cabinet. Drawing was carried out under isothermal conditions and at a crosshead speed of 100 mm/min.

In order to determine the drawability of the tapes an ink grid was stamped on the undrawn sample and the subsequent draw ratio λ of the sample was recorded as the ratio of the drawn length to the original grid length. *Figure 6* shows the maximum draw ratio that could be obtained for samples that had been swollen to different levels of W_s/W_p. In this paper we report results for the swollen UHMWPE tapes only, we found difficulty in drawing the lower molecular weight tapes to any significant draw ratio.

The mechanical properties of the drawn tapes were measured in terms of the room temperature tensile Youngs modulus and strength. Measurements were made on the samples of initial length 150–200 mm at a crosshead speed of 10 mm/min. The cross-sectional area of the sample was determined by weighing known lengths of drawn tape and assuming a density of 1000 kg m^{-3} for polyethylene.

Figures 7–9 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 now familiar progressive increase in properties with increasing draw ratio can be seen together with the fact that we are able to obtain a maximum modulus of 102 GPa and strength of 2.4 GPa. We feel that these figures are relatively conservative in that as yet we have not completed an optimization of the drawing conditions which could lead to further improvement in properties.

CHARACTERIZATION OF DRAWN MATERIAL

The development of anisotropy with drawing is clearly shown in the flat plate X-ray photographs shown in *Figure 10*. *Figure 10a* shows the swollen but unoriented precursor sample and *Figure 10b* shows the drawn material. Clearly anisotropy is developed solely in the drawing process. The enhanced orientation is also reflected in the melting behaviour of the tape which is shown in *Figure 11*. *Figure 11a* shows the scanning calorimeter (d.s.c.) trace of a swollen tape drawn ratio of 30× superimposed on a trace of the same sample being remelted. *Figure 11b* shows the curve for the workpiece swollen to W_s/W_p ratio of 17 and *Figure 11c* is a d.s.c. 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 characteristic melting peaks at 153.5°C, 160.6°C and 166.9°C where the absolute magnitude of the peak temperatures would depend on heating rate.

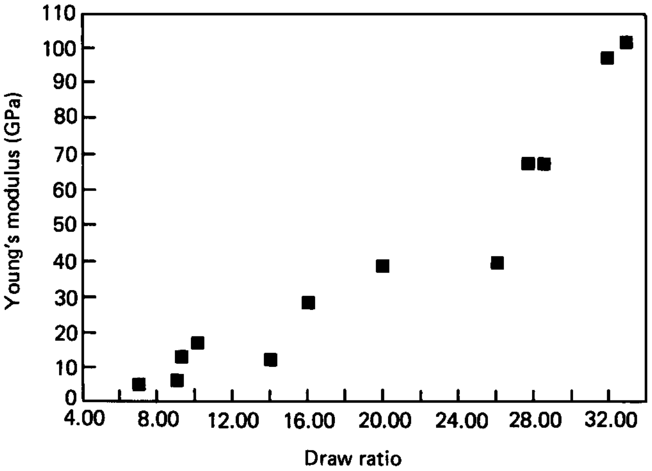

Figure 7 Youngs modulus *versus* draw ratio for Hostalen GUR tapes initial thickness of 0.3 mm immersed in dekalin for 2 min at 120°C

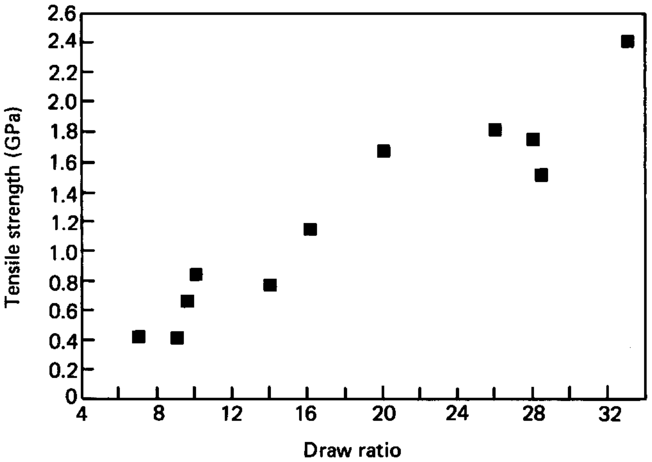

Figure 8 Strength *versus* draw ratio for Hostalen GUR tapes of initial thickness 0.3 mm immersed in dekalin for 2 min at 120°C

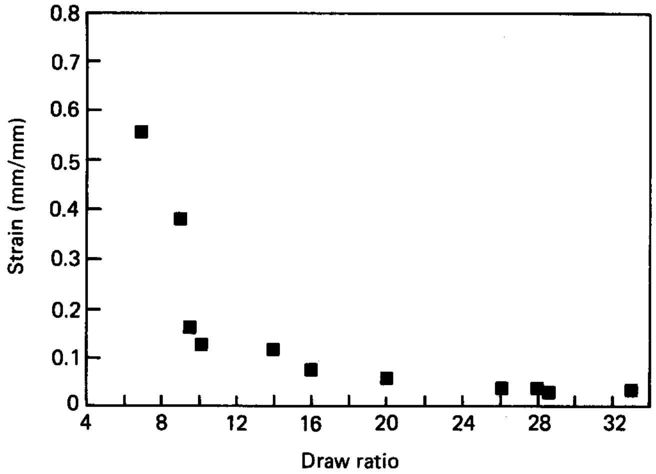

Figure 9 Maximum strain at failure *versus* draw ratio for Hostalen GUR tapes of initial thickness 0.3 mm immersed in dekalin for 2 min at 120°C

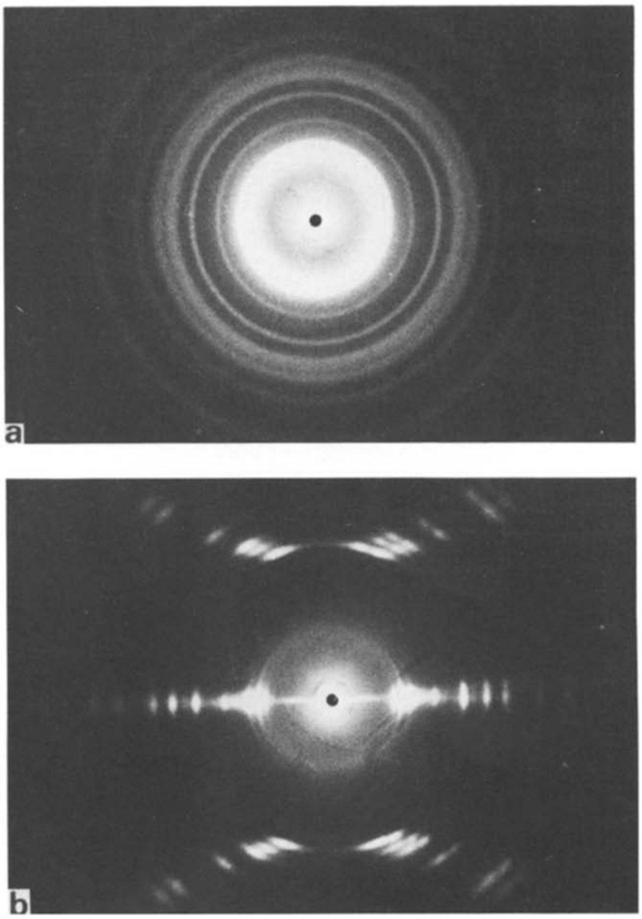

Figure 10 Wide-angle X-ray diffraction; (a) Swollen, dried and unoriented tape. (b) Swollen and drawn (draw ratio = 30). (draw direction is vertical)

MODELLING OF DRAWING BEHAVIOUR

The two areas of this study which merit detailed theoretical investigation are the swelling kinetics and the

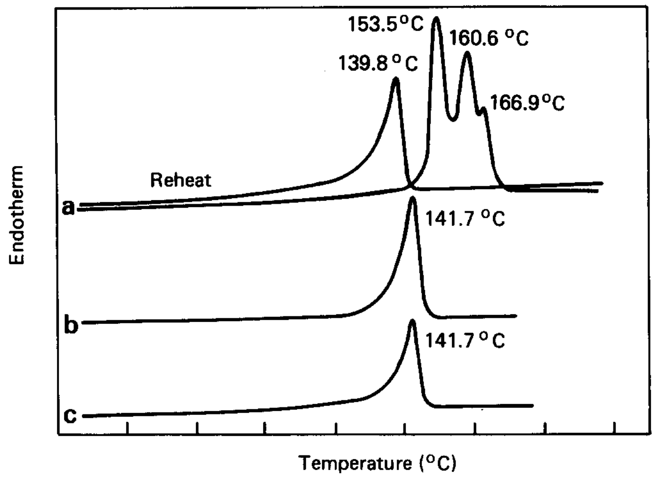

Figure 11 D.s.c. traces, carried out at a heating rate of 10 deg/min on approximately 2 mg samples; (a) Hostalen GUR tape swollen to $W_s/W_p=17$ and drawn ($\lambda=30$) with a superimposed trace of the same sample being reheated after cooling. (b) Tape which has been swollen to $W_s/W_p=17$ and dried without drawing. (c) Tape as received

subsequent drawing behaviour and in this paper we will limit ourselves to the drawing aspect.

Smith and Lemstra[4] 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 can define N_e the number of segments between entanglement points or equivalently M_c the molecular weight between entanglement points where $M_c=N_eM_0$, with M_0 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 points l_o as the root mean square end-to-end distance of the chain. In this way l_o would be related to N_e and a by,

$$l_o=N_e^{1/2}a \tag{1}$$

In an analogous way to a crosslinked rubber, deformation of the sample can be thought of in terms 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 $l=N_ea$.

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

$$\lambda_{max}=l/l_o=(N_ea/N_e^{1/2}a)=N_e^{1/2}=(M_c/M_0)^{1/2} \tag{2}$$

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

Graessley[11] relates the melt entanglement concentration to the entanglement concentration in solution by the relation

$$M_c=(M_c)_{melt}/v \tag{3}$$

where $(M_c)_{melt}$ is the molecular weight between entanglements in the melt (which can in principle be estimated from the linear viscoelastic plateau modulus of the material) and v is the volume fraction of the polymer. Combining equations (2) and (3) yields

$$\lambda_{max}=((M_c)_{melt}/M_0)^{1/2}v^{-1/2} \tag{4}$$

This equation originally presented by Smith, Lemstra and Booij[12] predicts that the maximum draw ratio increases with decreasing volume fraction of polymer. The argument relies on the existence of entanglements between chains and therefore would only be valid for $v>v^*$, where v^* is the critical volume fraction for chain overlap in solution.

The origin of equation (3) appears somewhat arbitrary and we believe that for our swelling procedure a modified equation may be appropriate. 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 equilibrium. 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[5,6].

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

$$\Delta G_1=RT(\ln(1-v)+v+\chi v^2) \tag{5}$$

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,

$$\Delta G_2=(\rho RTVv^{1/3})/M_c \tag{6}$$

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

$$\Delta G_1+\Delta G_2=0 \tag{7}$$

and

$$\ln(1-v)+v+\chi v^2+(\rho Vv^{1/3})/M_c=0 \tag{8}$$

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

$$M_c=-(\rho Vv^{1/3})/(\ln(1-v)+v+\chi v^2) \tag{9}$$

Combining equations (2) and (9), yields

$$\lambda_{max}=\{(-\rho Vv^{1/3})/[M_0\{\ln(1-v)+v+\chi v^2\}]\}^{1/2} \tag{10}$$

Generally we have been dealing with good solvents 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, then equation (10) can be approximated to,

$$\lambda_{max}=\{[2\rho Vv^{1/3}]/[M_0(1-2\chi)v^2]\}^{1/2} \tag{11}$$

or, ignoring χ

$$\lambda_{max}=(2\rho V/M_0)^{1/2}v^{-0.83} \tag{12}$$

Equation (12) is similar to the Smith, Lemstra and Booij equation (7) with the exception of the value for the power law controlling the v dependence, which in our derivation is -0.83 rather than -0.5.

Logarithmic plots of λ_{max} as a function of v are plotted for our experimental data in *Figure 12*. By carrying out a least square fit to a straight line we find a best fit power law index of 0.861 for specimens drawn at 120°C which is in good agreement with our equation (12). The good fit between the model and experimental results suggests that

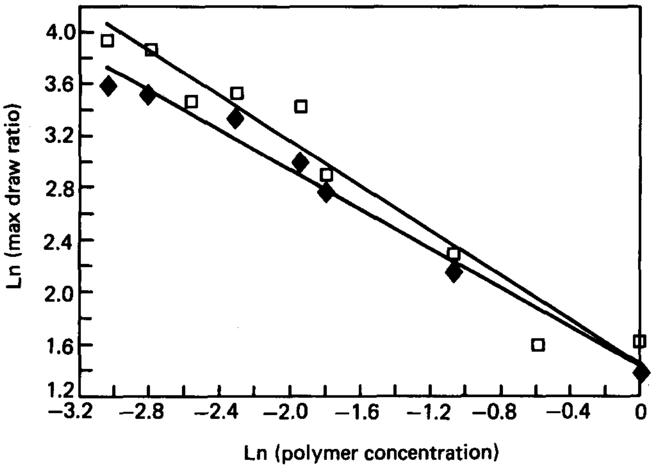

Figure 12 Ln of maximum draw ratio *versus* ln of the initial polymer concentration of swell drawn tapes; (□) draw temperature = 120°C; (◆) draw temperature = 90°C

there is some justification in our initial assumption that the solvent and polymer are at or near equilibrium. The process can readily be visualized as being continuous and one variant of a process line is shown schematically in *Figure 13.* 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.

The swell ratio W_s/W_p in excess of twenty that is reported in this paper is surprisingly high and suggests that the highest molecular weight chains are highly entangled before swelling. In addition the reptation time of these high molecular weight chains is certainly long and probably of the order minutes or greater implying that within the time scale of our experiments the chains are able to accommodate the solvent without losing molecular connectedness. The swelling kinetics certainly derserves closer experimental and theoretical attention.

The drawing behaviour of the swollen workpiece follows a similar pattern to the DSM process in that the drawability increases with increased initial solvent loading. This behaviour appears to be quantitatively consistent with our 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.

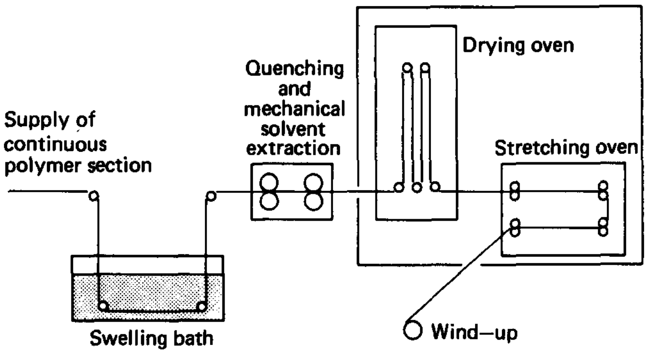

Figure 13 Schematic diagram of a swell drawing process

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