Effect of presolvent loading on the ultimate drawability of ultra-high molecular weight polyethylene

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Experimental data are presented on the variation of the plateau modulus for ultra-high molecular weight polyethylene (UHMWPE) as a function of solvent loading when the polymer is in the swollen state. The data show that the modulus follows the same form as that of a swollen crosslinked rubber. Using the plateau modulus as a measure of entanglement density we are able to correlate the subsequent solid state hot drawing of the preswollen UHMWPE with entanglement levels in the swollen material. A comparison between gel spinning and swell drawing data is made.

(Keywords: UHMWPE; swelling; entanglement; drawability; gel spinning)

INTRODUCTION

The gel spinning of ultra-high molecular weight polyethylene (UHMWPE) has received considerable attention since the discovery of the process in 1980[1]. A crucial aspect of the technology concerns the relationship between the ultimate drawability of the solid fibre and the solvent concentration at which the gel fibre is spun. Generally it has been found[2] that for gel spinning the maximum draw ratio of the fibre, λ_m, is related to the initial polymer volume fraction, ϕ_p, by the relation:

$$\lambda_{max} = \lambda^1_{max}\phi_p^{-1/2} \qquad (1)$$

where λ^1_{max} is the maximum draw ratio for the pure polymer. From this equation it is clear that in order to obtain a drawability of order 40, for example, it is necessary to spin at a low polymer volume fraction, i.e. for $\lambda^1_{max} = 4.0$, $\phi_p = 1.0\%$. The drawability, volume fraction relationship given by equation (1) has been associated with the reduction in entanglement of the UHMWPE during gel spinning and it is this aspect which is the primary concern of this paper.

Our objective is to determine an independent measure of entanglement concentration at different solvent loadings and relate this to drawability. We choose to adopt a swelling procedure[3,4] for preparing solvent laden samples rather than the solution process route generally followed. In relation to the experiments described in this paper, the swelling technique has certain experimental handling advantages when compared to solution processing. By measuring the plateau modulus of the swollen UHMWPE obtained from oscillatory linear viscoelastic measurements, we can obtain a measure of entanglement level as a direct function of solvent concentration and this measure can then be used to correlate drawability with the level of entanglement in the swollen polymer.

EXPERIMENTAL

The polymer used in this study was UHMWPE HG415 manufactured by Hoechst. Disc specimens, with radius of 12.5 mm, were cut from 0.58 mm thick tapes. The swelling procedure was as described previously[4] and the rheological measurements were performed on a Rheometrics dynamic spectrometer (RDS-II of Rheometrics Inc.). Parallel plate geometry was chosen for all the measurements. The procedure for rheological measurements was as follows. Firstly, the rheometrics spectrometer plates were preheated to the desired temperature and the plates accurately zeroed. Secondly, a single specimen was immersed in a swelling bath of solvent, (decalin) at 125°C for a preset time period; on removal it was rapidly weighed and transferred to another solvent bath of decalin at room temperature in order to slow down solvent loss. Diffusion of decalin into the polymer matrix is negligible at this temperature. Then the swollen polymer was quickly placed in the spectrometer. The small strain dynamic rate sweep experiment was commenced immediately after the oven reached the required temperature. The temperature used for the measurement was 130°C and the frequency range was $1 \leqslant \omega \leqslant 500$ rad s^{-1}. Measurements were made from high to low frequencies. These parameters were chosen in order to minimize the rate of solvent loss and also correspond to the optimized temperature of melting the gel crystallized polymer. In this way, a series of samples with a variety of solvent volume fractions can be measured and rate sweeps as a function of polymer volume fraction were constructed. For the solvent loadings described in this paper we have been able to show[5] that the concentration within the swollen sample is essentially uniform across the sample thickness. Samples swollen to the same swell ratio as used in the rheological measurements were quenched, dried and hot drawn in a manner previously described[3,4]. A single drawing temperature of 120°C was used at a single

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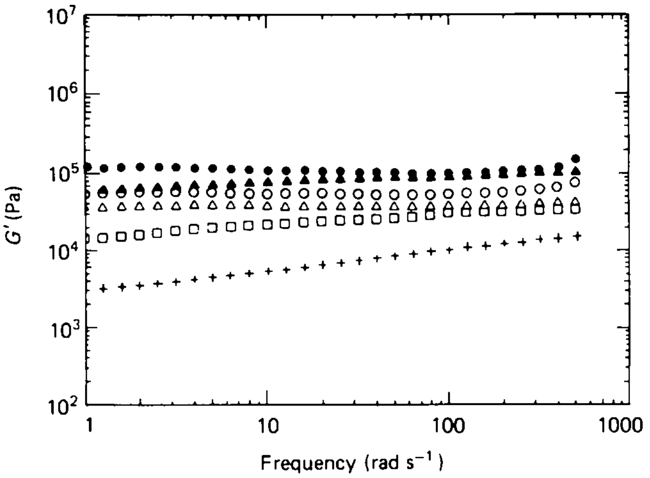

Figure 1 Dynamic rate sweeps for the storage modulus, G', data measured on samples of HG415 tapes of different polymer volume fraction, ϕ_p: +, 0.08; □, 0.11; △, 0.14; ○, 0.20; ▲, 0.26; ●, 0.31. Test temperature 130 C; strain 5%

drawing crosshead speed of 100 mm min^{-1}. The ultimate drawability under these drawing conditions and Young's modulus of the material could then be determined[4].

RESULTS

Results shown in *Figure 1* represent the storage modulus G' data as a function of angular frequency and polymer volume fraction. It is seen that at any one solvent loading the storage modulus G' is roughly independent of frequency above about 100 rad s^{-1}; however, the absolute value of G' rapidly decreases with increasing solvent loading. From the data presented we are able to determine a 'plateau modulus' for each solvent concentration using a mean value of G' between 100 and 500 rad s^{-1}. The value of the G' plateau modulus is plotted in *Figure 2* as a function of the solvent volume fraction ϕ_p.

The plot shown in *Figure 2* is double logarithmic and the data are matched to the relation established by Treloar[6] for the equilibrium swelling of crosslinked rubbers:

$$G_{\phi_p} = G'_0 \phi_p^{5/3} \tag{2}$$

The fit between the experimental data and swollen crosslinked rubber equation is surprisingly good. This implies that at each stage of swelling in the UHMWPE a local equilibrium is reached in terms of the entanglement density and solvent concentration. The value of G'_0 used here[5] is 1.06 MPa.

The relation between maximum drawability and solvent concentration given by equation (1) has been derived[2] using two base equations. It is well known that PE in the molten state exists as highly entangled chains that are themselves essentially in a random configuration. The molecular weight M_e of the polymer segments between these entanglement junctions can be determined from the melt plateau modulus of the polymer, G'_0, given by:

$$G'_0 = \frac{\rho RT}{M_e} \tag{3}$$

where ρ is the polymer density, R the universal gas constant and T the absolute temperature. If it is assumed that entanglement junctions are fixed, the distance between these junctions can be thought of in terms of the root mean square end-to-end distance, l_0, of the random chain between entanglement points; this is given by $l_0 = a \times r^{1/2}$, where r equals the number of repeat units between entanglement junctions and a the link length of each repeat unit, r is equal to M_e/M_0, where M_0 is the equivalent molecular weight of a statistical chain segment. Smith *et al.*[2] then speculate that the entanglement level within the melt is trapped in the material during crystallization and that the subsequent drawability of the material is controlled by the drawability of this entanglement network. If the network was fully drawn, the limiting end-to-end distance between entanglements would be $a \times r$ yielding a maximum draw ratio λ_{max} of:

$$\lambda_{max} = \frac{ar}{ar^{1/2}} = r^{1/2} = \left(\frac{M_e}{M_0}\right)^{1/2} = \left(\frac{\rho RT}{M_0 G'_0}\right)^{1/2} \tag{4}$$

If solvent is present Smith *et al.* used the Graessley equation[7] coupling G'_{ϕ_p} to ϕ_p:

$$G'_{\phi_p} = G'_0 \phi_p \tag{5}$$

Replacing G'_0 in equation (4) by G'_{ϕ_p} given by equation (5):

$$\lambda_{max} = \left(\frac{\rho RT}{M_0 G'_0}\right)^{1/2} \phi_p^{1/2} \tag{6}$$

Equation (6) shows a $\phi_p^{-1/2}$ dependence for the concentration dependence of the maximum draw ratio. Using either the Treloar equation for the relation between G' and ϕ_p, or the equation derived by Mackley and Solbai[3], or the direct experimental equation given in this paper, substitution into equation (4) yields:

$$\lambda_{max} = \left(\frac{\rho RT}{M_0 G'_0}\right)^{1/2} \phi_p^{5/6} \tag{7}$$

In *Figure 3* the experimentally determined data on maximum draw ratio are plotted as a function of ϕ_p together with the Mackley–Solbai equation (7) and the

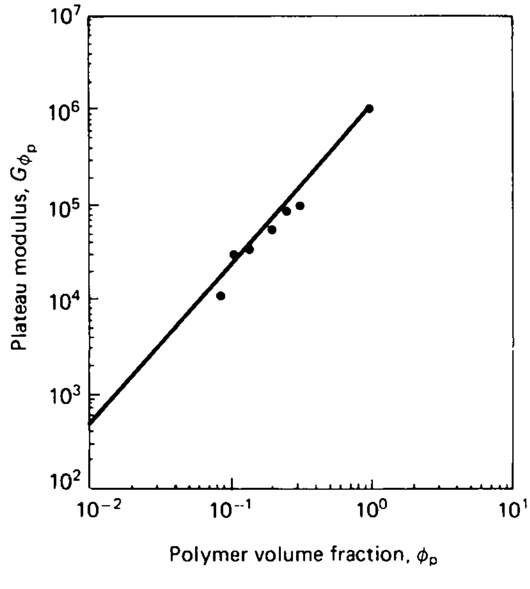

Figure 2 Plateau modulus, G_{ϕ_p} *versus* polymer volume fraction, ϕ_p, obtained from the data in *Figure 1*. ●, Calculated from *Figure 1*; —, predicted by Treloar[6]

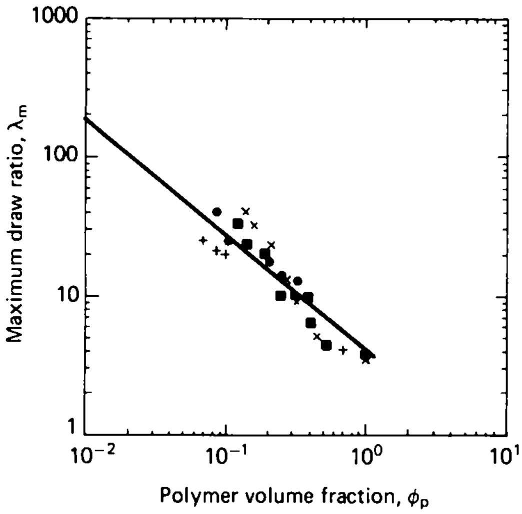

Figure 3 Comparison of maximum draw ratio, λ_m, *versus* initial polymer volume fraction, ϕ_p, obtained from tensile stretching and calculated from both G' data in *Figure 2* (●) and the model prediction by Mackley and Solbai[3](———). The drawing conditions: draw temperature 120°C; cross head speed 100 mm min^{-1}. Sample thickness: +, 0.33 mm; ×, 0.58 mm; ■, 0.89 mm

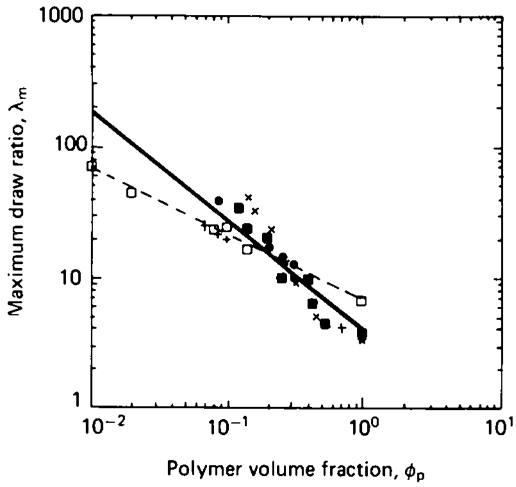

Figure 4 Comparison of maximum draw ratio, λ_m, *versus* initial polymer volume fraction, ϕ_p, between model predictions by Mackley and Solbai[3] and Smith *et al.*[2]. ●, Calculated from experimental G' data; , predicted by Mackley and Solbai[3]; □, data from Smith *et al.*[2]; ---, predicted by Smith *et al.*[2]. Sample thickness: +, 0.33 mm; ×, 0.58 mm; ■, 0.89 mm

value of λ_m obtained using the G' data given in *Figure 2*. The general agreement is reasonable and we estimate experimental errors in both λ_m and ϕ_p to be of order 5%.

The results reported here support the conclusion that at any swelling concentration the entanglement level in swollen UHMWPE correlates closely with that of the equilibrium swelling of a crosslinked rubber when the crosslink density is free to change with swelling time. In addition the drawability can be correlated with the entanglement level within the swollen polymer.

COMPARISON OF GEL SPINNING AND SWELL DRAWING

Figure 4 shows a comparison of data on swell drawing reported in this paper with data on gel spinning reported by Smith *et al.*[2]. The maximum draw ratio is plotted as a function of polymer volume fraction. The results show that the Smith *et al.* equation (6) appears to agree well with the gel spinning data, and the Mackley Solbai equation (7) agrees reasonably well with the swell drawing data. The differences between each model plot arrives from the different dependence of G' as a function of ϕ_p. The swell draw G' data are consistent with our experimental findings.

At this stage it is not clear to us why swell drawing and gel spinning should appear to follow different concentration dependences. One obvious difference in the two routes is that in the swelling case the material receives no fluid processing and it is plausible to visualize a local thermodynamic equilibrium being reached between polymer and solvent. In the case of gel spinning, swelling, dissolution and large strain fluid processing take place and it is possible that the fluid processing affects equilibrium conditions. The differences in behaviour may be important because the results indicate that in order to achieve a certain draw ratio, less solvent loading is required by the swell draw process than in gel spinning. The preferred commercial process will operate in the top right-hand corner of *Figure 3* and from the data presented, the swell draw process appears closer to that goal than the gel spinning process.

CONCLUSION

Our results seem to support the original idea of Smith *et al.*[2] that drawability is related to entanglement levels prior to crystallization; the independent measurements of the plateau modulus as a measure of entanglement level also support this view. There are, however, two other factors which may influence the drawability of the UHMWPE: one is common to both swell drawing and gel spinning and the other is particular to swell drawing alone.

The common factor concerns the development of porosity in the material with the introduction of solvent. Several workers[8,9] have reported the highly porous nature of both the swollen and gel spun fibres. This porosity does not appear to influence the room temperature drawing behaviour of the dried material but it is plausible that the porosity may influence drawability above the transition temperature of 80°C. The feature unique to the swelling process concerns the possibility of solvent concentration profiles within the polymer. Gao[5] has undertaken a detailed study of the diffusion kinetics of decalin solvent in UHMWPE and under the solvent loadings reported here it is anticipated that the solvent concentration will be essentially uniform across the sample. However, it is possible that under certain conditions surface concentration may be higher than the bulk concentrations and this aspect may improve the subsequent ultimate drawability of the material. The latter aspect is amenable to experimental investigation but the decoupling of entanglement levels and porosity seems difficult to achieve experimentally.

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REFERENCES

1 Smith, P. and Lemstra, P. J. *J. Mater. Sci.* 1980, **15**, 505
2 Smith, P., Lemstra, P. J. and Booij, H. C. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 877
3 Mackley, M. R. and Solbai, S. *Polymer* 1987, **28**, 1111
4 Gao, P., Mackley, M. R. and Nicholson, T. M. *Polymer* 1990, **31**, 237
5 Gao, P. *PhD Thesis*, University of Cambridge, UK, 1990
6 Treloar, L. R. G. 'Physics of Rubber Elasticity', Clarendon, Oxford, 1975
7 Graessley, W. W. *Adv. Polym. Sci.* 1976, **16**, 58
8 Kalb, B. and Pennings, A. J. *Polymer* 1980, **21**, 3
9 Prevorsek, D. C. 'Polymer Liquid Crystals', Academic Press, New York, 1982