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Extrusion processing of ultra-high molecular weight polyethylene; a new method for the production of high performance structures

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Abstract

We report preliminary findings relating to a method of processing ultra-high molecular weight polyethylene (UHMWPE) in order to obtain extrusions that possess significant molecular orientation and improved mechanical properties. We also show that the method can be used to produce oriented extrusions of composite materials consisting of glass or carbon fibres in a matrix of UHMWPE.

Background

It is well known that the zero shear viscosity of polymers increases with molecular weight, MW, by the relation $\eta = (MW)^n$, where n is about 3.4 (1). With the increasing value of MW for any molecular weight distribution the viscosity of the polymer melt progressively increases and for polyethylene when MW > 10^6 the material becomes essentially undeformable by viscous processing procedures. The high molecular weight, and consequent high entanglement concentration also means that the material can only be plastically deformed to a small degree. It is possible to extrude UHMWPE in constant cross-section dies but the dominant relative motion only occurs as slip at the wall and extrusion into a contraction of as little as 2/1 presents major processing difficulties.

It has been clearly shown by the pioneering work of Ward (2) and Smith and Lemstra (3) that in order to obtain high molecular orientation in polyethylene it is necessary to draw the material to draw ratios (DR) in excess of, say, 20. The deformation can either be applied by tensile drawing (2,3), or by hydrostatic extrusion with die drawing (4). However, because of the difficulties in processing UHMWPE the hydrostatic extrusion of polyethylene has so far been limited to those with normal molecular weight distributions (10^4-10^5) i.e. Rigidex 006-60 ($\bar{m}_n$=25,000 $\bar{m}_w$=135,000). The work carried out by Smith et al. (5) has shown that by processing material that has been solidified in the gel state it is possible to subsequently hot draw the material to very high draw ratios. The results of experiments performed by us (6) support the conclusion that the enhanced drawabilty is plausibly related to the decrease in entanglement concentration for polymers crystallised from the solvent laden gel state rather than from the melt. It is the object of this paper to demonstrate that gel crystallised polyethylene can also be used with great advantage in the solid state extrusion process.

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We have developed a procedure by which gel crystallised polymer can be extruded to high draw ratios through a convergent die. The process produces extrusions of highly oriented UHMWPE and, in addition, if desired, co-extrusion of reinforcing fibres with the UHMWPE can also be achieved.

The process has essentially three steps:

(1) gel preparation

(2) crystallisation and solvent removal

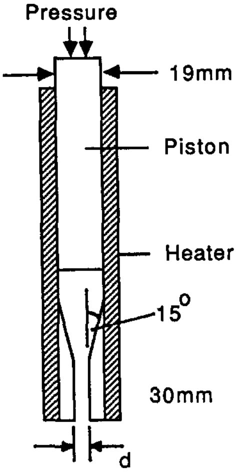
(3) extrusion

Each of the steps was carried out batchwise, but it is not difficult to envisage that they could, if required, be carried out continuously.

Experimental

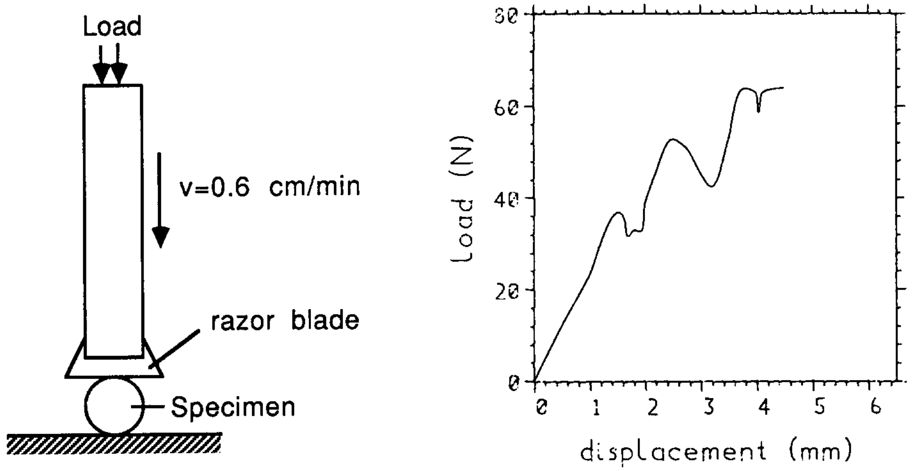
The polymer used was Hifax 1900 with $\bar{m}_w > 10^6$ and the solvent decalin (decahydronaphthalene). A polymer gel solution was obtained by adding the polyethylene powder to the decalin bath at 80°C and heating further to 140°C whilst mechanically stirring. The onset of gelation occurred at approximately 105°C at which point the stirring was stopped and the solution left for 30 minutes before being air cooled to room temperature to allow crystallisation. The crystallised gel was then mechanically squeezed to remove most of the solvent before being fragmented in a Thermomix 2200 blender, and dried in a vacuum oven at 70°C for about 24 hours. A gel crystallised polyethylene containing about 5w/w% solvent was then obtained (i.e. 99.95% of the original solvent was removed).

The material was then extruded through a circular converging die using a Davenport rheometer with a barrel diameter of 19mm, as illustrated schematically in figure 1, to produce an oriented UHMWPE structure. Temperatures between 100-140°C were utilised and pressures up to 255MPa.



Schematic view of Davenport rheometer
Figure 1

The stiffness of the extrudate was measured using a 3-point bending test on a JJ tensile testing machine, whilst the hardness /toughness was measured using a technique we have developed of monitoring the force required to drive a razor blade through a specimen at a constant speed. This apparatus is illustrated in figure 2a and a typical trace shown in figure 2b.



a) Schematic of razor blade test apparatus
b) Typical trace of load required to cut oriented specimen vs. displacement of blade into specimen

Figure 2

The load required to make the first notch in the sample gave a measure of the hardness of the specimen, whilst the area under the curve gave an indication to the toughness.

Our extrusion technique has also made it possible for us to extrude glass and carbon fibre filled UHMWPE specimens. The gel was made up in the usual manner and chopped fibres (typically of a few mm in length) were added to the solution at the same time as the polymer. Even dispersion was easily maintained by the stirring and there were no clumping problems.

Results and Discussion

The pressure required to extrude various samples is listed in table 1. It was not possible to continuously extrude all the samples but where an upper limit for the pressure is given it was necessary to ram extrude by working up to the limit, reversing the motor, and then working back up to the limit. Alternatively, the extruded material was observed to flow out of the die at the limit load and this was accompanied by a reduction in the measured ram load.

The table shows that concentration and temperature are important variables. The extrusion pressure increases with increasing concentration of the original gel suggesting that entanglement concentration plays a major part in the ease of deformation. Increasing temperature also eases extrusion. In general it seems that this method offers a route to a high performance product. It was also observed that the residual content of

gel conc %	fillers	EDR	temp °C	extrusion pressure MPa
0.5	none	20	100	110
1.0	none	20	100	170
1.5	none	20	100	>220
0.5	none	20	110	90
1.5	none	20	130	140
1.5	none	25	130	>220
1.0	15v/v% glass	15	100	170
1.0	15v/v% glass	25	100	>245
1.0	30v/v% glass	15	100	>220
1.0	30v/v% glass	5	100	>220
1.0	30v/v% glass	5	130	86

Extrusion conditions required to extrude a number of gel crystallised specimens. The upper limit of the rheometer was 255MPa.

Table 1

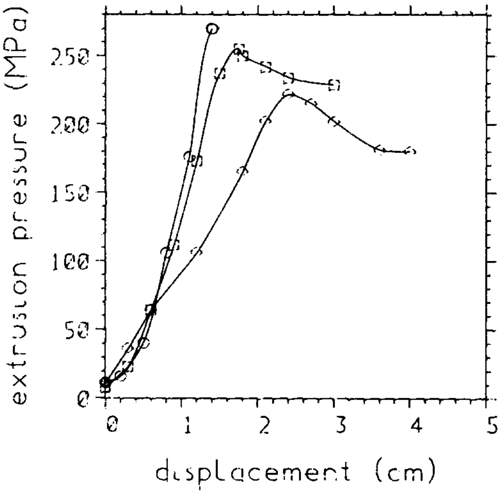
solvent is important in assisting the extrusion process, but may be detrimental if too much is present as the solvent in the sample becomes compressed and causes an explosive, unstable extrusion. The maximum extrusion draw ratio (EDR) reached was 25 as this was limited by the maximum capacity of the rheometer (255MPa).

The Young's modulus was found to increase with EDR, the values for a 1.0% gel crystallised sample without fillers were

EDR	E (GPa)
5	8.0
15	13.6
20	19.9
25	23.6

The presence of fibre additives appears to improve the Young's modulus of the specimens. A specimen which was formed from a 0.5% gel crystallised sample with 30v/v% glass fibres had a Young's modulus of 37GPa. The hardness and toughness was also improved by the addition of fibre additives. Our results showed that the force required to notch the specimen increased with increasing fibre concentration, but that above about 25v/v% the extrudates became brittle. It was found, by microbeam X-ray photographs and SEM micrographs of the billets and the extrudates, that the extrusion process caused high orientation of both the UHMWPE matrix and the glass or carbon fibres that were used as fillers.

It was also noted that the gel crystallised polymer, which was compressible, was compacted in situ prior to the entry to the die. This was reflected by the initial increase of ram load with displacement as the polymer underwent compression strain hardening. The load was observed to decrease as the compacted polymer yielded and subsequently extruded through the die. The presence of small amounts of glass fibres (2v/v%) reduced this effect as the glass fibres filled the voids in the structure reducing the compressibility of the bulk polymer. However, large amounts of glass fibre (30v/v%) made the process more difficult as the material was less easy to deform. Increasing temperature facilitated the extrusion. These effects are illustrated in figure 3.



Comparison between unfilled gel crystallised extrudates at 110°C (◇), glass-filled gel crystallised extrudates at 110°C (○) and at 120°C (□) at EDR=20.

Figure 3

Conclusion

Previous methods of solid state extrusion of polyethylenes have been limited to lower molecular weights, and have only been able to operate batchwise because of the need to use preformed billets. Our method is suitable for UHMWPE and could be carried out continuously using a reciprocating ram with a hopper feed if required. The process has yet to be optimised but these initial results indicate that this route offers a viable method to the production of high performance polyethylene structures.

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