polymer report

The fabrication of microporous polyethylene having a negative Poisson's ratio

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A novel thermoforming processing route has been developed that produces a microporous form of ultra high molecular weight polyethylene that demonstrates large negative Poisson's ratios. The microstructure consists of nodules interconnected by fibrils. Poisson's ratios as low as -1.2 have been obtained, depending on the degree of anisotropy in the material.

(Keywords: polyethylene; microporous; negative Poisson's ratio; fabrication; compaction; sintering; extrusion)

INTRODUCTION

Until recently, it was generally believed that all materials had a positive Poisson's ratio (ν). For isotropic materials, the theoretical range is $-1 \leqslant \nu \geqslant +\frac{1}{2}$ and for anisotropic materials $|\nu_{ij}| \leqslant (E_i/E_j)^{1/2}$ where E_i and E_j are the major and minor orthotropic Young's moduli. However, in 1987 a novel foam was fabricated that demonstrated a negative Poisson's ratio[1]. The effect has been examined and has been shown to be due to the microstructural geometry of the foam structure and not the intrinsic properties of the foam material itself[2–4].

Such materials are of interest for a number of reasons. First, the negative ν effect may be of direct use in specific applications, for example in fasteners and seals. Second, the existence of a negative ν can result in enhancements in other mechanical properties, such as shear modulus, indentation resistance or plane strain fracture toughness[1,5]. Third, the complexity of the microstructures producing the effect may also produce other phenomena, associated, for example, with internal rotational degrees of freedom as seen in Cosserat or micropolar materials[6–8]. To avoid the cumbersome phrase 'materials with a negative Poisson's ratio', the term auxetic materials has been used[9].

The disadvantage of the foam-based auxetic materials is their intrinsically low stiffness, making them unsuitable for structural applications. The discovery that a particular form of microporous poly(tetrafluoroethylene) (PTFE)[10] has a negative Poisson's ratio suggested an alternative approach to the fabrication of auxetic materials. Extensive examination of the microporous PTFE has shown that it exhibits a negative ν using a different mechanism to that seen in the auxetic foams. A model has been developed for this mechanism[11] and successfully applied to PTFE[12]. It has been possible to accurately predict changes in ν as a function of strain. This results from changes in the microstructure during the deformation process. These changes are reversible and repeatable.

One important consequence of this work is the hypothesis that the auxetic behaviour is entirely due to the complex microstructure found in the microporous PTFE and not to any intrinsic mechanical property of the PTFE itself.

In this paper it is shown how a similar microstructure to that seen in the PTFE material can be produced in ultra high molecular weight polyethylene (UHMWPE), leading to negative Poisson's ratios. The details of the processing route are described and values for the negative Poisson's ratios obtained are given.

REVIEW OF CURRENT PROCESSING ROUTES FOR UHMWPE AND PTFE

Many varied processing routes are available for UHMWPE such as compression moulding, flow moulding, transfer moulding, sintering and ram extrusion. Of these, the latter two are the most relevant for this work and so will be considered here prior to descriptions of the novel processing route developed to produce the required microstructure.

Powder metallurgical techniques have been used to process UHMWPE as a cheaper and less cumbersome alternative to conventional polymeric processing operations. These techniques involve compaction of the powder followed by free sintering and may be used in conjunction with ram extrusion. Compaction of the powder may take place at room temperature[13,14] or at elevated temperatures that are less than the polymer melting point[15,16], known to be around 140°C from d.s.c. analysis. Temperatures used range between 90°C[15] and 110°C[16], while compaction pressures vary between 0.04 GPa[16] and 0.2 GPa[15].

The next stage of the process is sintering which is usually carried out above the melting point of the polymer in the range 130–200°C[13,14]. The optimum sintering temperature to produce material with properties which compare favourably with UHMWPE processed by normal means has been found to be just above the melting temperature[14].

Compacted, sintered UHMWPE may be further

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processed by extrusion techniques[15,16]. For example, Zachariades *et al.*[15] extruded compacted billets at 90°C and 0.11 GPa and at 128°C and 0.23 GPa, whereas Pawlikowski *et al.*[16] have used solid state coextrusion to further process their material at a temperature of 110°C and at a crosshead speed of 0.5 mm min^{-1}.

The crucial difference between the earlier work on UHMWPE and the work to be described below is that all previous work has had the aim of producing a solid, highly compacted homogeneous polymer that is highly oriented and very stiff along the oriented direction. The aim here is to generate a particular type of microporous, preferably isotropic, network structure exhibiting a negative Poisson's ratio.

The PTFE material previously investigated and shown to exhibit a negative Poisson's ratio[10,12] is also fabricated initially by compaction and sintering[17]. This is a necessary starting point for all PTFE solids as the material degrades below its melting point. The microporous PTFE is fabricated from this solid former by a rapid axial stretch process at elevated temperature[18]. Strain rates of up to 50 s^{-1} are used, with a common value being 5 s^{-1} (ref. 18). This produces a fibrillated structure along the axis of the specimen. The resulting combination of fibrils and nodules then provides the microstructure[10] demonstrating a negative ν.

In the method to be described here for UHMWPE a 'rapid-stretch' method was not required as expansion of the material occurred naturally during the extrusion process. The resulting fibrillar structure was much more nearly isotropic with any preferential fibril orientation tending to lie in directions radial to the extrusion axis.

EXPERIMENTAL

Processing route for auxetic UHMWPE

A novel thermoforming processing route has been developed in order to produce UHMWPE material with a negative Poisson's ratio[19]. Two grades of UHMWPE powder were used (GUR 415 and GUR 412), which were provided by Hoechst. The processing route consists of three distinct stages—compaction, sintering and extrusion—which all took place in a specially designed extrusion rig (*Figure 1*).

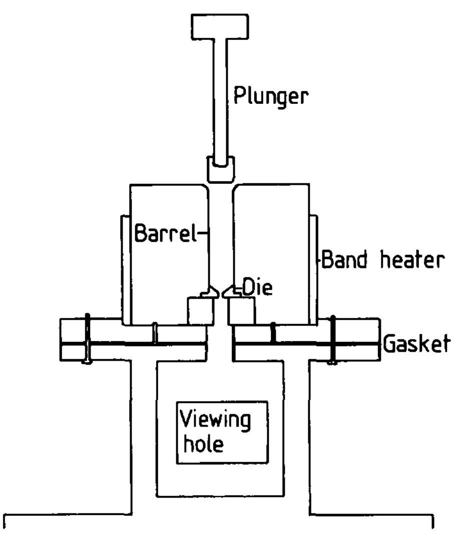

Figure 1 Schematic of the extrusion rig

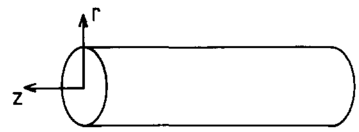

Figure 2 Schematic of the extrudate showing the axis system used

The first stage of the process is to ensure that the powder is compacted and the following optimum compaction conditions have been established. The extruder was fitted with a blank die and heated to 110°C. The barrel of the extruder, which has a diameter of 15 mm and length 80 mm, was filled with UHMWPE powder and the entire system allowed to come to equilibrium for 10 min. Then, the extruder plunger was driven by a Schenk mechanical testing machine into the barrel at a rate of 20 mm min^{-1} until a pressure[16] of 0.04 GPa was reached and this was maintained for 20 min, resulting in a well formed rod.

The compacted rods were then subjected to a range of sintering and extrusion conditions, with possible variables being the die diameter, temperature and extrusion rate. The effect of varying each condition was examined, with die diameters varying from 5 to 10 mm, temperatures varying from 100 to 190°C and the extrusion rates varying up to a maximum of 1000 mm min^{-1}. The axial strain rate used varied up to 0.42 s^{-1}. Extensive experimentation has led to optimum extrusion conditions being established, which result in a microstructure similar to that seen in the microporous PTFE that has a negative ν.

Measurement of ν

The extrudates were subjected to compression testing in two directions (either axial or radial) and the strains in the material were measured using a simple photographic technique developed in-house. From these measurements, the Poisson's ratio can be determined in two directions (*Figure 2*):

$$\nu_{zr} = -\frac{\varepsilon_r}{\varepsilon_z}$$

where the load is applied in the z direction.

$$\nu_{rz} = -\frac{\varepsilon_z}{\varepsilon_r}$$

where the load is applied in the r direction.

By twisting the specimens about their axis, it is also possible to check that the material properties are axisymmetric. Typical applied compressive strains varied between 0.027 and 0.125.

Microscopic examination of the UHMWPE

Samples of the extruded material were taken from the extrudates and mounted on aluminium stubs. These were then gold coated using a sputter coater to establish a well formed conducting path from the specimen surface to the aluminium stub. The samples were observed by SEM at magnifications of up to ×1250 to examine their microstructure.

RESULTS

Processing conditions used to produce a negative ν in UHMWPE

After extensive experimentation, the following processing conditions were defined which produced a negative

ν in UHMWPE. This was generated by sintering a compacted rod of GUR 415 powder at 160°C for 20 min. The plunger was then driven by a Schenk mechanical testing machine into the extruder barrel at a rate of 500 mm min^{-1}, forcing the material through a 5 mm diameter die. Initial work was carried out using an extruder barrel of diameter 15 mm. It is interesting to note that the material expands after being forced through the 5 mm diameter die to a diameter of around 10 mm, with the resultant expanded material having cup-and-cone fractures at regular intervals along its length. Obviously, these fractures are a major problem in terms of producing a consistent material and therefore, although the desired effect was obtained, this case was not ideal. Further changes were made and it was found that if the diameter of the extruder barrel is reduced from 15 to 10 mm whilst retaining all the other processing conditions established as optimum, the extrudate consists of smooth, continuous material with cup-and-cone fractures restricted to the specimen ends. Once again, the material has expanded after being forced through the 5 mm diameter die to a diameter of ~9 mm.

Measurement of ν

Due to the small size of the specimens generated, it was not possible to measure strains in standard tensile specimens. The results are therefore subject to a degree of inaccuracy. However, any effects due to small specimen size, for example, associated with end effects, would tend to reduce the magnitude of the resulting measured Poisson's ratio. The results presented here, therefore, represent, at worst, a conservative estimate of the negative ν value.

The values of Poisson's ratio measured by the photographic technique for 16 specimens extruded from the 10 mm diameter barrel and processed using the optimum conditions defined above, are listed in *Tables 1* and *2*. Both compression directions (*Figure 2*) are considered. (It was found that the specimens were axially symmetric so the direction of r need not be specified.)

Considering firstly compression testing in the r, or radial, direction, the range of Poisson's ratio values measured varies between 0.00 and −1.24 (see *Table 1*). It can be seen from these results that the Poisson's ratio values are very strain dependent with the largest variations observed at low strains. The magnitude of the Poisson's ratio falls with applied strain. At the highest strains, ν_{rz} values of zero are obtained. This is possibly due to the onset of plastic deformation when the material is subjected to large strains.

Table 1 Values of ν_{rz} for material compressed in the r direction[a]

Specimen no.	ν_{rz}	Applied compressive strain
1	−1.24	0.027
2	−0.64	0.028
3	−0.36	0.033
4	−0.33	0.037
5	−0.21	0.056
6	−0.13	0.059
7	−0.09	0.067
8	−0.10	0.071
9	−0.17	0.086
10	−0.17	0.088
11	−0.10	0.097
12	0.00	0.103
13	0.00	0.111
14	0.00	0.125

[a] Error ~ ±0.02

Table 2 Values of ν_{zr} for material compressed in the z direction[a]

Specimen no.	ν_{zr}	Applied compressive strain
3	+0.1	0.050
5	0.0	0.070
6	0.0	0.090
11	+0.1	0.040
15	+0.1	0.010
16	+0.1	0.041

[a] Error ~ ±0.05

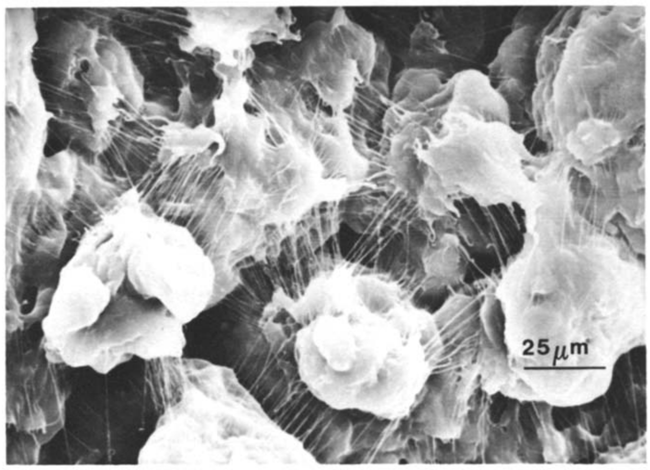

Figure 3 Micrograph of the auxetic UHMWPE

Considering now compression in the z, or axial, direction, for these tests, in order to avoid specimen buckling, measurements were carried out on either individual discs or on very short sections extracted from the extruded specimens. As a result, the systematic error is significantly higher. Results from six sections are quoted and the Poisson's ratio values for these tests vary between 0.0 and +0.1 (see *Table 2*).

Microscopic examination of the UHMWPE

Samples of the auxetic material were observed by SEM at magnifications of up to ×1250 to examine their microstructure. *Figure 3* is a typical micrograph revealing that the microstructure consists of an open network of particles (nodes or nodules) interconnected by fibrils. The optimum microstructure is qualitatively similar to that seen in PTFE[10]. However, node shape and relative fibril lengths are different. At other, non-optimum processing conditions, the fibrillar structure is not seen and the nodes flow or deform and are aggregated with varying degrees of adhesion. An example of the microstructure of such a specimen is shown in *Figure 4*. This specimen was compacted as for the optimum specimens but was extruded at a lower temperature of 110°C (following the work of Pawlikowski *et al.*[16]), a much reduced extrusion rate of 20 mm min^{-1} and through a larger die which had a diameter of 12.5 mm.

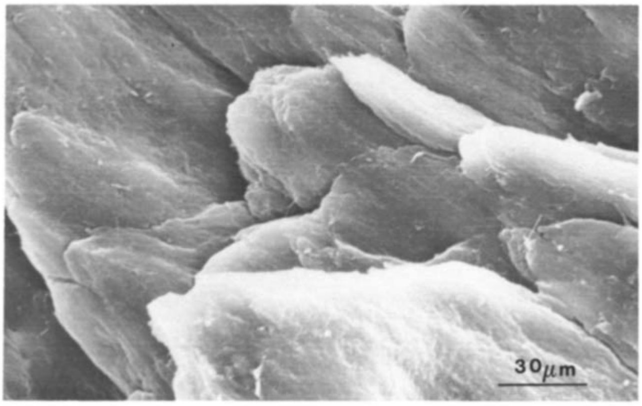

Figure 4 Micrograph of a non-optimum structure

DISCUSSION

A processing route has been developed that can produce auxetic polyethylene. This route is significantly different to that used to produce auxetic PTFE. In the latter case fibrillation is induced by a high rate stretch in the axial direction[18]. In the former case fibrillation occurs by radial expansion on leaving the extruder die. It is tempting to relate this to the common phenomenon of die swell in polymers. However, the extrudate is clearly not molten, and the mechanism is not yet understood.

Qualitatively, the microstructure seen for both auxetic polymer materials is similar but there are some notable differences. First, the nodules are more nearly spherical in the auxetic UHMWPE. Second, the fibrillar structure is more isotropic. This is borne out by the measured values of the Poisson's ratios in the radial direction, which for auxetic UHMWPE is never greater than -1.24, while for auxetic PTFE it can be as large as -12 (ref. 10). For many applications an isotropic material is preferred so values near -1 are optimal. The low magnitude for ν_{zr} may be explained by the fact that the specimens are insufficiently long to be free of end effects, in which case the specimens are unable to contract freely and the values quoted may be a significant underestimate of ν_{zr}.

Table 1 illustrates very clearly that there is a large dependence on strain for ν_{rz}, particularly at low strain. The present test method does not allow continuous strain control which would result in a full strain history of the auxetic UHMWPE being recorded. A strongly strain-dependent Poisson's ratio was a feature of the PTFE material. Whether this feature in auxetic UHMWPE can be explained using a similar model[11,12] is currently under investigation.

CONCLUSIONS

A novel thermoforming processing route consisting of three separate stages—compaction, sintering and extrusion—has been developed that produces an expanded UHMWPE microstructure that demonstrates negative Poisson's ratios. The material produced is homogeneous and continuous and has Poisson's ratio values varying from 0.00 to -1.24, depending on applied strain, in the radial direction and approximately zero in the axial direction.

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