JOURNAL OF MATERIALS SCIENCE **35** (2000) 1023–1030

Hydrostatically extruded HAPEX^{TM}

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Hydroxyapatite reinforced high density polyethylene composite (HAPEX^{TM}) has been developed for bone substitution. To improve its mechanical properties, HAPEX^{TM} was hydrostatically extruded at different extrusion ratios after compression moulding. Substantial increases in the tensile and flexural properties of both unfilled polyethylene and HAPEX^{TM} were achieved. It was evident that the higher the extrusion ratio, the stiffer and the stronger the extruded rods. The ductility of HAPEX^{TM} was also significantly enhanced by hydrostatic extrusion. Hydrostatically extruded HAPEX^{TM} possesses mechanical properties that are within the bounds for human cortical bone, which indicates its potential for load-bearing skeletal implant applications.

1. Introduction

Various engineering materials, including metals and ceramics, have been routinely used in orthopaedic surgery as replacements for bone in a variety of procedures ranging from bone grafting to total-hip replacement. However, these implant materials possess much higher modulus values than that of cortical bone [1]. Such a modulus mismatch causes bone to resorb at the bone-implant interface, which leads to implant instability, and revision surgery is often required subsequently.

Bonfield *et al.* pioneered the use of bioactive particles as the reinforcement in a polymer matrix to produce bone substitutes [2], considering the fact that cortical bone itself at the ultra-structural level is a composite consisting of nanometer-size apatite crystals (5 nm × 5 nm × 50 nm) and collagen fibres. Hydroxyapatite [HA: $Ca_{10}(PO_4)_6(OH)_2$], which closely resembles bone apatite, was chosen to reinforce polyethylene for developing a bone analogue [3]. The ductile polyethylene allowed the incorporation of a high percentage of bioactive particles in the polymer, which is essential for achieving desired bioactivity of the composite. With hydroxyapatite reinforced polyethylene (now designated as HAPEX^{TM}), it has been anticipated that mechanical properties of the composite would match those of cortical bone and hence the problem of bone resorption would be avoided.

The manufacturing process of HAPEX^{TM} consists of blending, compounding and centrifugal milling, followed by either compression or injection moulding. Composites with up to 45 vol% (i.e. 73 wt %) of HA can be made routinely and the HA particles were found to be evenly distributed in polyethylene [4]. Such a uniform distribution of the bioactive phase in a composite is essential for the mechanical as well as biological performance of implants. Different mechanical properties can be achieved by varying the mean particle size and particle size distribution of HA, and the polyethylene matrix [5].

Furthermore, by varying the amount of HA in HAPEX^{TM}, a range of mechanical properties of the material and biological response to the material can be obtained. It was found through *in vivo* studies that a minimum amount of HA (approximately 20 vol%) in

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TABLE I Mechanical properties of skeletal tissues

Skeletal tissue	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at fracture (%)
Cortical bone	7–30	50–150	1–3
Cancellous bone	0.05–0.5	10–20	5–7
Articular cartilage	0.001–0.01	10–40	15–50
Tendon	1	80–120	10

the composite is required for bone apposition and bone bonding to occur in a mechanically lightly loaded implant [6]. An increase in the HA volume percentage leads to increases in both the Young's modulus and tensile strength of HAPEX^{TM}, with a corresponding decrease in the strain to fracture. A ductile-brittle transition exists at about 40 vol% of HA for HAPEX^{TM}, in which case the Young's modulus is 4.29 GPa, which approaches the lower bound for cortical bone (Table I). This composite can still be readily shaped with a scalpel in the operating theatre, enabling the implant to be made an exact fit for the patient [7]. HAPEX^{TM} has already been used clinically for orbital floor reconstruction [8] and otologic and maxillo-facial surgery [9].

HAPEX^{TM} processed through the conventional route is suitable for low load bearing applications in the human body. For major load bearing clinical applications, it is necessary to increase substantially its stiffness and particularly its strength while retaining reasonable ductility.

It has long been recognised that molecular orientation in a polymer results in the significant enhancement in both stiffness and strength along the orientation direction [10]. The effects are particularly evident with polyethylene due to its simple molecular structure. The increase in tensile modulus was correlated with the average longitudinal crystal thickness in the ultra-oriented polyethylene [11]. Ward *et al.* used several techniques to induce molecular orientation in different grades of polyethylene, such as tensile drawing [12], die drawing [13] and hydrostatic extrusion [14], and investigated major factors controlling the mechanical properties of drawn or extruded polyethylenes [15, 16]. Among these established technologies, hydrostatic extrusion was shown to increase substantially the tensile strength and modulus of polyethylene [14]. It was found that the polyethylene molecules were oriented and the spherulites transformed into the fibre structure in the extruded material, which accounted for the enhancement in stiffness and strength of polyethylene [11, 17].

Hydrostatic extrusion is of particular interest for enhancing mechanical properties of HAPEX^{TM}, as it is capable of producing oriented structures in brittle materials [18, 19]. Another advantage of using hydrostatic extrusion is that, compared to other techniques such as tensile drawing, it can provide oriented polymers with large geometrical dimensions and hence offers potential in the manufacture of suitably sized, strong and stiff implants which contain a polymeric phase. Therefore, HAPEX^{TM} manufactured through the conventional route was further hydrostatically extruded [20], and the structure and properties obtained are reported in this paper.

2. Materials and methods

2.1. Materials production

Synthetic HA (Grade P88, Plasma Biotal Ltd, UK) and a high density polyethylene (HDPE: Rigidex HM4560XP, BP Chemicals Ltd, UK) were used to produce HAPEX^{TM} containing 40 vol% of HA. Grade P88 HA has a median particle size of 4.14 μm and the particles are small compacts of HA crystallites [4]. Rigidex HM4560XP is an ethylene hexene co-polymer with less than 1.5 butyl branches per 1000 carbon atoms. Its weight average molecular mass ($\bar{M}_w$) is quoted by the manufacturer to be 225000 and the number average molecular mass ($\bar{M}_n$) to be 24000.

2.1.1. Billet preparation

HAPEX^{TM} pellets were manufactured via the established route [4]. The billets (60 mm in length and 12 mm in diameter) for hydrostatic extrusion were produced by the method described previously [20].

Some HAPEX^{TM} billets were also produced by injection moulding (SL2 Air Operated Machine, J.B.Engineering, UK). The moulding temperature was 180°C and the rod dimensions were 90 mm in length and 10 mm in diameter.

2.1.2. Hydrostatic extrusion

The technology for the hydrostatic extrusion of polyethylene (and hence HAPEX^{TM} in the current study) was described previously [16]. Briefly, a billet of the solid polymeric material is surrounded by a fluid and made to flow through a die by applying pressure to the fluid. Practically, it involves surrounding a billet with a fluid of appropriate viscosity, heating up the liquid (and hence the billet) to a temperature below the polymer melting point, and extruding the billet through a convergent die by pressurising the fluid. The main process variables are the nominal extrusion ratio *Rn*, defined as the ratio of the billet cross-sectional area to the die bore cross-sectional area, and the die cone semi-angle α. The die used had a cone semi-angle of 15° and the bore diameters were 1.8, 2.5, 3.0 and 3.5 mm, respectively, depending on the extrusion ratio to be achieved ($Rn = 5:1, 8:1$ or $11:1$). The billets produced by compression or injection moulding were given the nominal extrusion ratio of 1 : 1. They were machined with a 15° nose to create an initial pressure seal for the hydrostatic extrusion. At the end of the nose a constant diameter stub was also machined, which protruded a few millimeters into the die. To keep the extruded rod straight and to provide a means of sensing its displacement during extrusion, a cable was attached to the constant-diameter stub and a small load (about 100 g) applied. The other end of the cable drove a rotary potentiometer to obtain the displacement signal. The back 3 mm of the billets were machined to a larger diameter to act as a plug and prevent the violent release of pressure and hot fluid at the end of the run.

The pressurising fluid used was castor oil (J. L. Seaton, Hull, UK). Billets of HDPE and HAPEX^{TM} were coated with two layers of a rubber-like adhesive

"Evostick" (Evode Ltd, Stafford, UK) to avoid direct contact between the polymer and the pressurising fluid, which can cause stress cracking of the polymer. Each applied layer of Evostick was allowed to dry for several hours prior to hydrostatic extrusion.

2.2. Materials characterisation

2.2.1. Distribution of hydroxyapatite

The distribution of HA particles in the HDPE matrix was investigated for HAPEX^{TM} after compression or injection moulding and hydrostatic extrusion. The polished composite surfaces, prepared by a standardised method [4], were lightly gold coated and examined under a JEOL 6300 scanning electron microscope (SEM).

2.2.2. Differential scanning calorimetry (DSC)

The melting and crystallisation temperatures of the polyethylene matrix before and after hydrostatic extrusion were measured using a Perkin Elmer DSC 7 differential scanning calorimeter. The heating and cooling rates were 10°C/min, and 2 to 10 mg of the material were analysed each time.

2.2.3. Tensile testing

In studying the tensile drawing and hydrostatic extrusion behaviour of polymers, it was found that the Young's modulus provides a good practical guide to the effectiveness of the deformation process. Therefore, tensile testing was initially used for the assessment of mechanical properties of hydrostatically extruded HDPE and HAPEX^{TM}.

The extruded rods were cut to 50 mm in length and machined into specimens to conform to ASTM E466. They were subsequently embedded at each end in an epoxy resin to facilitate gripping. Tensile tests (at room temperature) were performed on an Instron 6025 machine at a crosshead speed of 0.5 mm/min. The specimen extension was measured with a spring-loaded knife type extensometer and this result was used to calculate the Young's modulus of extruded HDPE or HAPEX^{TM} at the strain of 0.05%. The specimens were tested to failure, and hence the tensile strength and fracture strain were determined. Some rods were tensile tested unmachined in order to investigate a possible core-skin structure. In these cases, only the Young's modulus could be obtained because the specimens slipped in the epoxy resin blocks above certain stress levels (normally greater than 90 MPa).

2.2.4. Flexural testing

With an increasing amount of extruded rods becoming available, mechanical properties of hydrostatically extruded HDPE and HAPEX^{TM} were mainly assessed using flexural tests. A minimum of four specimens were tested for each condition. The three point bending tests were performed according to ASTM 790, with the rods in their as-extruded diameters. The ratio of specimen gauge length to its diameter was always greater than 15. All the tests were carried out at room temperature using an Instron TT-CM machine at the cross-head speed of 0.5 mm/min. Three properties, namely flexural modulus (FM), flexural strength (FS) and flexural ductility (FD), were obtained using the following formulae [21]:

$$\mathrm{FM} = \frac{4}{3}\frac{WL^3}{\pi\delta D} \tag{1}$$

$$\mathrm{FS} = \frac{8WL}{\pi D^3} \tag{2}$$

$$\mathrm{FD} = \frac{6D\delta}{L^2} \tag{3}$$

where W is load, δ is deflection, L is specimen gauge length and D specimen diameter. The term "ductility" here refers to the maximum strain of the specimen if it failed during testing. Some rods did not break in bending and the load-deflection curve exhibited a peak load. In these cases the ductility were measured at the maximum stress. Fracture or peak loads were used to calculate the flexural strength.

2.2.5. Fracture surface observations

Tensile fracture surfaces of hydrostatically extruded HAPEX^{TM} were gold coated and examined under a JEOL 6300 scanning electron microscope (SEM).

3. Results

3.1. Hydrostatic extrusion

A preliminary study suggested that HAPEX^{TM} required a higher extrusion temperature than that for linear polyethylene to ensure its successful hydrostatic extrusion, and hence 115°C was used for both HDPE and HAPEX^{TM} throughout the current investigation. The extrusion rate was maintained at approximately 1.5 mm/min. The extrusion pressure, however, varied from 19 to 207 MPa, depending on the extrusion ratio and the material being extruded. It was found that the Evostick coating on the billets peeled off during extrusion and did not go through the die. The diameter of hydrostatically extruded rods ranged from 1.6 to 3.5 mm, which was dependent on the extrusion ratio and diameters of the billet and the die bore.

Generally, after the preliminary trial runs, fault-free rods were produced by hydrostatic extrusion. However, defects such as helical fracture and localised distortion did occasionally occur. The reasons for such defects have been discussed elsewhere [20].

3.2. Properties

Fig. 1 shows the tensile stress-strain curve of HAPEX^{TM} hydrostatically extruded at $Rn = 5:1$. HAPEX^{TM} samples extruded at higher extrusion ratios exhibited similar mechanical behaviour. Under the tensile load, the extruded rod deformed with a gradually decreasing tangent modulus up to a certain stress level above which a near-constant, but significantly

TABLE II Tensile properties of hydrostatically extruded HDPE and HAPEX™

Sample code	Process[a]	HA volume (%)	Extrusion ratio	Young's modulus (GPa)	Tensile strength (MPa)
CM0.1	Betol	0	1 : 1	0.65	17.89
PC0.20	Non-Betol	0	5 : 1	1.58	67.35
PC0.100	Betol	0	5 : 1	2.59	61.24
PC0.24	Betol	0	8 : 1	4.08	158.2
CM40.1	Betol	40	1 : 1	4.29	20.67
PC40.1	Betol	40	5 : 1	5.89	64.78
PC40.7	Betol	40	8 : 1	9.91	91.23
PI40.2[b]	Betol	40	8 : 1	11.4	80.84

[a]Indicating whether the material was processed through the Betol compounding extruder prior to compression moulding of billets.
[b]The sample was hydrostatically extruded using an injection moulded billet.

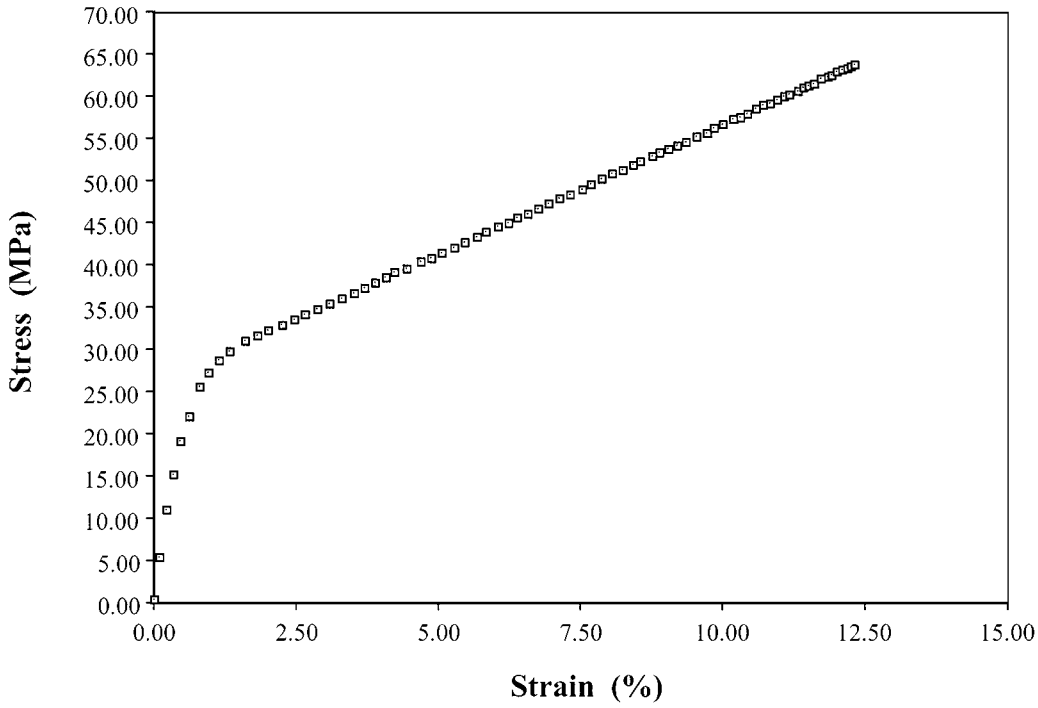


Figure 1 Tensile stress-strain curve of HAPEX™ hydrostatically extruded at the extrusion ratio of 5 : 1.

lower, tangent modulus was maintained. The rod usually fractured in this near-constant modulus region, the fracture point depending on the volume fraction of HA and the extrusion ratio. Tensile testing results for HDPE and HAPEX™ after hydrostatic extrusion are listed in Table II. It is evident that higher extrusion ratios have led to higher Young's modulus and tensile strength for both HDPE and HAPEX™. The fracture strain of HAPEX™ was also substantially increased by hydrostatic extrusion, rising from 2.6% at $Rn = 1 : 1$ to 9.4% at $Rn = 8 : 1$. It was found that higher modulus values could be obtained from un-machined (i.e. without removal of skin of the rod) specimens than from machined (i.e. with the skin being removed) specimens.

Table III shows flexural properties of the materials tested. It can again be seen that hydrostatic extrusion of HAPEX™ has produced improvements in the flexural stiffness and strength of over 100%, accompanied by increases in ductility of at least 400%. The flexural modulus and strength of hydrostatically extruded HAPEX™ appeared to increase with increasing extrusion ratio, although a leveling-off seemed to take place towards the highest extrusion ratio attempted in the current study.

TABLE III Extrusion pressure and flexural properties of hydrostatically extruded HDPE and HAPEX™

HA volume (%)	Extrusion ratio	Extrusion pressure (MPa)	Modulus (MPa)	Strength (MPa)	Ductility (%)
0	1:1	—	1.1	23	6.2
0	5:1	19	2.2	52	9.0
0	8:1	51	2.2	48	9.6
40	1:1	—	4.7	32	1.4
40	5:1	41	7.2	73	7.0
40	8:1	94	9.0	88	6.5
40	11:1	207	10.8	79	4.1

Tensile and flexural properties obtained for hydrostatically extruded HAPEX™ are comparable at each extrusion ratio (Tables II and III). The results listed in Table III suggest that optimum mechanical properties can be achieved at $Rn = 8 : 1$ for HAPEX™. Both tensile and flexural tests have shown the hydrostatically extruded HAPEX™ possesses strength and stiffness

that are within the bounds for cortical bone, together with a superior ductility (Tables I–III).

3.3. Structure

A homogeneous distribution of HA particles in the HDPE matrix was found in both the centre and edge of hydrostatically extruded HAPEX^{TM} rods at all extrusion ratios. Comparing the SEM micrographs taken from polished composite surfaces (perpendicular as well as parallel to the extrusion direction) with results obtained previously [4], it appeared that hydrostatic extrusion did not alter the dispersion and distribution characteristics of HA in HAPEX^{TM} which had been achieved after compounding.

The DSC thermograms of HDPE before and after being processed through the compounding extruder exhibited similar melting endotherms, indicating that the compounding process did not cause any significant morphological change in the polymer (Fig. 2a). Compression moulding of the polyethylene resulted in a moderate increase in the melting temperature (Fig. 2b). A further increase was detected after hydrostatic extrusion at $Rn = 5:1$ (Fig. 2c), consistent with an oriented polymer morphology. The polyethylene rods with extrusion ratios of 5 : 1 and 8 : 1 displayed similar melting behaviour.

Fig. 3 shows the melting behaviour of HAPEX^{TM} before and after hydrostatic extrusion. Compression moulding of the composite gave rise to an increase in the endotherm peak temperature (Fig. 3a), as it was the case for the unfilled polymer. But this temperature was lower than unfilled HDPE (128°C vs. 131°C). Substantial increases in melting temperature were induced by hydrostatic extrusion with $Rn = 5:1$ (Fig. 3b) and $Rn = 8:1$ (Fig. 3c). However, a higher extrusion ratio ($Rn = 11:1$) did not result in an additional increase of the endotherm peak temperature.

SEM examination of tensile fracture surfaces revealed that a core-skin structure, as shown in Fig. 4a, existed in hydrostatically extruded HAPEX^{TM}. The skin may not be concentric with the centre of the rod as a varying thickness of the skin was found around the core. Fig. 4b shows the skin area of the fracture surface of HAPEX^{TM} extruded at $Rn = 8:1$.

4. Discussion

Various methods including die drawing and hydrostatic extrusion have been used to increase substantially the stiffness and strength of polymers. However, die drawing was found to be unsuitable for HAPEX^{TM} [22], due to premature fracture caused by cavity formation during the drawing process. In a finite element analysis of HAPEX^{TM} [23], with simple assumptions of linear elasticity and perfect bonding between the reinforcement and the matrix, it was shown that the maximum direct stress concentration is radial stress at the pole: this is the concentration of applied stress pulling the interface apart. The maximum shear stress concentration is around $\theta = 45^{\circ}$ in the negative direction. This maximum is close to, but not precisely at, the position of maximum von Mises stress in the matrix. Therefore,

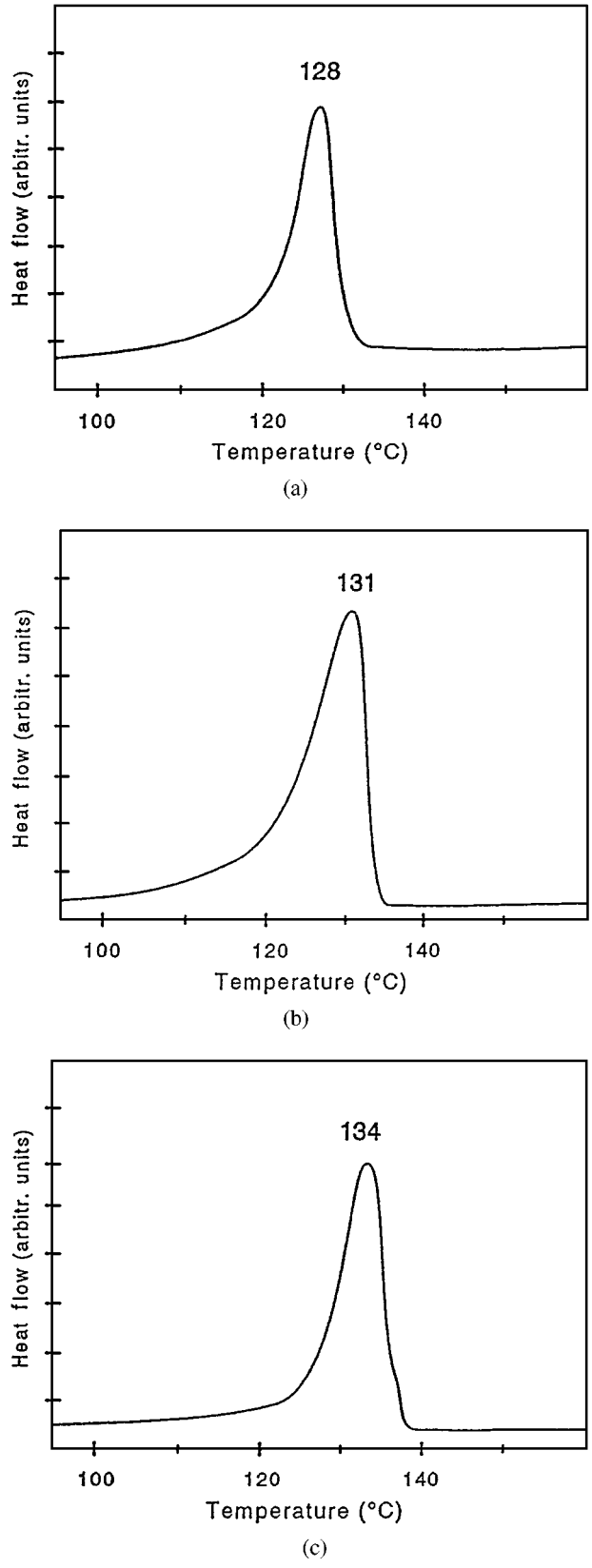


Figure 2 DSC thermograms of HDPE: a) after compounding; b) after compression moulding; c) after hydrostatic extrusion at $Rn = 5:1$.

when a mechanical bond exists between the reinforcing particles and the matrix, as in the case of HAPEX^{TM}, interfacial debonding will inevitably occur under tensile stress, which leads to cavitation around the particles. Although a stronger bond was formed between the filler and the matrix with chemical coupling of HAPEX^{TM}, cavitation following interfacial debonding

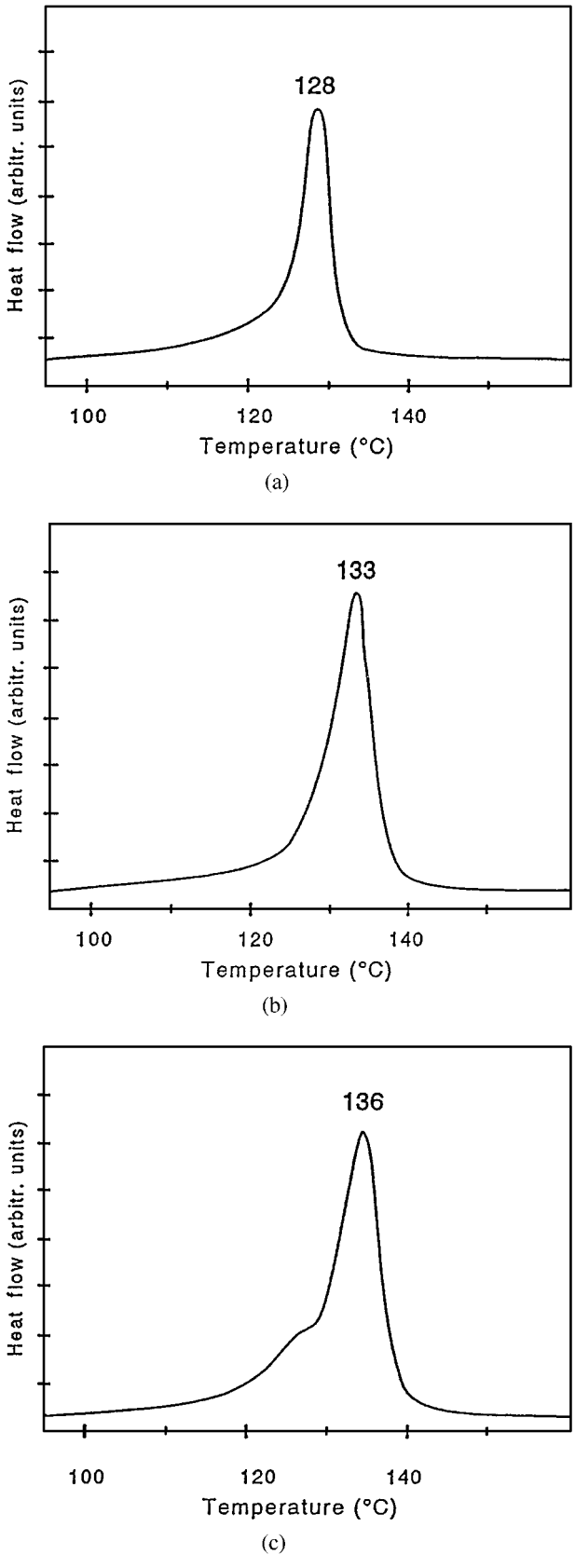


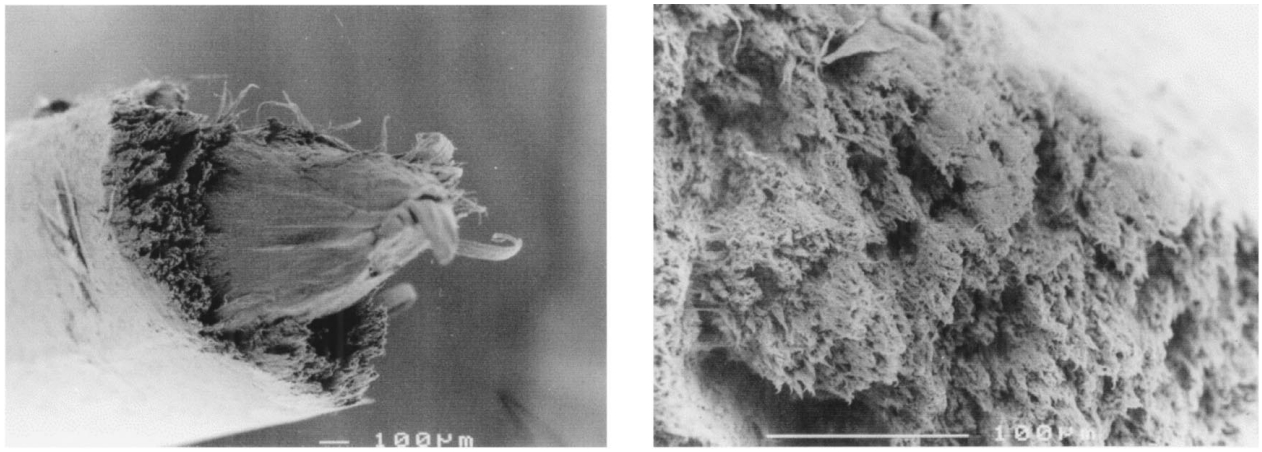
Figure 3 DSC thermograms of HAPEX^{TM}: a) after compression moulding; b) after hydrostatic extrusion at $Rn = 5:1$; c) after hydrostatic extrusion at $Rn = 8:1$.

was still observed during tensile testing [24]. Hence die drawing, which employs a tensile stress field, is not suitable for highly filled polymers. These results are similar to those obtained previously for the die drawing and hydrostatic extrusion of polyoxymethylene filled with glass fibres [25]. However, it is shown through the current study that hydrostatic extrusion can be successfully employed to produce particulate filled polyethylene with high strength and stiffness. In the case of either die drawing or hydrostatic extrusion, the billet is heated to a sufficiently high temperature to allow flow, but below the polymer melting point in order to obtain a polymeric structure with a high degree of molecular orientation. Hydrostatic extrusion has the distinctive advantage of being capable of producing oriented products from brittle materials, because the deformation occurs in a totally compressive field.

Previous studies suggested that linear polyethylene should be extruded at 100°C for optimum balance between the increasing deformability of the material and loss of product properties due to annealing effects at higher temperatures [26]. The extrusion temperature of 115°C used in the current study is necessary for ensuring successful extrusion and good quality products. With 40 vol% of HA, HAPEX^{TM} is a highly filled polymer containing approximately 70 wt% of the ceramic particle. Its ability to resist deformation is considerably greater than the unfilled HDPE at the extrusion temperature, and hence much higher extrusion pressure is required (Table III). During hydrostatic extrusion, there is a shear component of work which increases with increasing die angle. Provided small die angles are used, like 15° in the current study, it is fairly reasonable to neglect the effects of shear deformation on the distribution of strains in the product.

Most researchers used a set-up which operates by moving a ram, or by pumping a fluid into a vessel at a constant rate for hydrostatic extrusion. This causes the pressure to increase with time until extrusion commences. The pressure required to maintain the steady-state extrusion is often considerably lower than the initial breakthrough pressure. In the current study, operation of the extrusion process is that of maintaining a constant pressure, allowing this to control the extrusion rate. This technique is not suitable for most metals because it requires a high degree of strain rate sensitivity. With HDPE or HAPEX^{TM}, however, the strain rate dependence is high, and hence their hydrostatic extrusion has been successful. During the steady-state extrusion of HAPEX^{TM}, the extrusion pressure is normally 10–20% lower than the initiation pressure.

The liquid surrounding the billet in hydrostatic extrusion is required to fulfil two functions: (i) to transmit and convert the load from the pump or plunger into a hydrostatic pressure around the billet, and (ii) to lubricate the interface between the sliding surfaces of the billet and the die. The selection of this pressurising liquid is important as it should have a low viscosity but does not cause stress cracking of the product. With the Evostick coating, stress-cracking of polyethylene seems to be avoided. Both compression moulding and injection moulding have been shown to be suitable for the fabrication of billets. However, the extrusion characteristics and mechanical properties of the extruded rods are not significantly affected by the type of moulding. It was noted that the surface finish is also important, as blemishes on the billet may be carried through the die on to the product.



(a) (b)

Figure 4 Tensile fracture surface of HAPEX^{TM} hydrostatically extruded at the extrusion ratio of 8 : 1: (a) a general view; (b) the skin region.

The billet does not need to be of the same shape as the die bore. Therefore, square or hexagonal billets can be extruded through a round die bore, and conversely extruded products with square or other cross-sections can be obtained by using non-circular die bores. It has been shown that tubular and non-circular sections of polyethylene can be successfully hydrostatically extruded [27]. Hence hydrostatic extrusion of HAPEX^{TM} implants with desired cross-sections is possible, albeit processing parameters need to be optimised. Obviously, by extruding billets of non-constant section, such as tapered or stepped billets, the extrusion ratio, and consequently the properties of the material, can be varied along the length of the product, which itself is of a constant cross-section.

For hydrostatic extrusion, fluid-to-fluid extrusion (i.e. with a fluid back pressure in the second pressure chamber from the die exit) can be employed to avoid cracking of the product and to increase the ductility of the product (sometimes with increases in strength as well). It was reported that for products manufactured at the same extrusion ratio but into different fluid back pressures, the ductility of the products was permanently increased by the use of a high back pressure [19]. Therefore, it may be possible to use such a technique to increase the ductility of HAPEX^{TM}.

Hydrostatic extrusion not only improves the mechanical properties of both filled and unfilled polyethylene in the extrusion direction, but also changes their tensile behaviour. For the extruded rods, there are two distinctive regions as far as their tensile curves are concerned (Fig. 1). Such tensile characteristics differ greatly from the behaviour of both filled and unfilled polyethylene prepared without hydrostatic extrusion. Compression moulded HDPE undergoes yielding and necking under tension, while compression moulded HAPEX^{TM} with 40 vol% of HA exhibits a near-linear tensile stress-strain curve prior to fracture [4]. It is evident for HDPE or HAPEX^{TM} that the higher the extrusion ratio, the stiffer and the stronger the extruded rod (Table II). With an extrusion ratio of 8 : 1, the Young's modulus and tensile strength of HAPEX^{TM} are 2.6 and 4.4 times higher than those of compression moulded material. An additional benefit of hydrostatic extrusion is the substantial increase in fracture strain (a measure of ductility) which is far greater than that of human cortical bone (9.4% vs. 0.5–3.0%). It is important to observe, by comparing the mechanical properties shown in rows 2 and 3 of Table II, that materials need to be processed through the compounding extruder in order to achieve larger property improvements.

Flexural tests show that the stiffness and strength of hydrostatically extruded HDPE and HAPEX^{TM} follow similar ascending trends, namely a major increase with $Rn = 5 : 1$, followed by a moderate increase up to $Rn = 8 : 1$ with little change thereafter up to $Rn = 11 : 1$ (Table III). The ductility of HAPEX^{TM} decreases sharply with an increasing amount of HA [4], but the application of hydrostatic extrusion has led to substantial increases in ductility, with all the extruded HAPEX^{TM} rods displaying a ductility above the maximum fracture strain of cortical bone.

As was shown extensively in the past, the melting temperature of drawn or extruded polymers is indicative of the degree of molecular orientation [27, 28]. Therefore, the melting behaviour as well as the progression of the stiffness and strength of HDPE and HAPEX^{TM} can be qualitatively understood on the grounds of an increasingly oriented matrix as the extrusion ratio increases. Hydrostatic extrusion of HDPE with the extrusion ratio from $Rn = 5 : 1$ to $Rn = 8 : 1$ corresponds to a 100% improvement in flexural stiffness and strength as compared to the non-extruded HDPE, and an increase in the melting temperature. The matrix molecular orientation is enhanced by the incorporation of HA, as is indicated by the data in Tables II and III. For extrusion ratios above 8 : 1 any additional deformation which has taken place through morphological changes in the HAPEX^{TM} has little effect on the melting behaviour of the matrix and hence on the stiffness and strength of the composite. The melting range seen in Fig. 2a is somewhat lower than expected for polyethylene, owing to Rigidex HM 4560XP being a co-polymer.

Extrusion ratios above 8 : 1 are attainable for both HDPE and HAPEX^{TM}, notwithstanding a drastic increase of the extrusion pressure (Table III). There

appear to be no significant gains in the mechanical properties for HAPEX^{TM} with such high extrusion ratios. Mechanical testing results (Tables II and III) indicate that an optimum combination of properties can be obtained for HAPEX^{TM} (with 40 vol% of HA) at an extrusion ratio of 8 : 1. HAPEX^{TM} with higher HA content (such as 50 vol%) may improve the bioactivity of the composite, but can cause considerable production difficulties during compounding [4], while not providing superior mechanical properties.

At the microstructural level, the investigation into the distribution of HA particles in hydrostatically extruded HAPEX^{TM} rods has revealed the same (or at least highly similar) dispersion and distribution characteristics of HA in the polymer matrix as that in compression moulded samples, both exhibiting good dispersion and uniform distribution of the HA particles. However, at the macrostructural level, a core-skin structure can possibly exist in HAPEX^{TM} processed using the current technological parameters, which has been verified by both mechanical testing and fracture surface examination. The skin is stiffer than the core, which accounts for higher modulus values of un-machined specimen than those of machined specimen from the same sample. The thickness of the skin is probably influenced by both the HA volume fraction and the extrusion ratio.

Hydrostatically extruded HAPEX^{TM} possesses mechanical properties which are within the bounds for human cortical bone. Therefore, it can be used for major load bearing applications in the human body. Currently, it is ideal that implants are made without removing the skin of hydrostatically extruded HAPEX^{TM} to avoid any uncertainty regarding their structure and mechanical properties.

Past experience has shown that there is an optimum combination of extrusion temperature and pressure that leads to the highest stiffness of linear polyethylene [16, 26]. Therefore, future research in die design and optimisation of the extrusion process may lead to the elimination of the core-skin structure and further improvements in the mechanical properties of HAPEX^{TM}.

5. Conclusions

Hydroxyapatite reinforced high density polyethylene composite (HAPEX^{TM}) containing 40% by volume of hydroxyapatite particles has been hydrostatically extruded at different extrusion ratios. Higher extrusion ratio leads to greater stiffness and strength of the material. The composite after hydrostatic extrusion possesses mechanical properties that are within the bounds for human cortical bone together with a significantly improved ductility. Therefore, HAPEX^{TM} further processed via hydrostatic extrusion shows great promise for major load bearing applications.

Acknowledgements

The authors would like to thank their colleagues at both the IRC in Biomedical Materials and the IRC in Polymer Science and Technology for assistance and helpful discussions. Support from the UK EPSRC for the IRC programmes is gratefully acknowledged.

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Received 1 October 1997
and accepted 22 July 1999