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The role of pressure annealing in improving the stiffness of polyethylene/hydroxyapatite composites

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The effect of the combination of pressure annealing and subsequent hydrostatic extrusion on some mechanical properties of composites of hydroxyapatite in a polyethylene matrix is examined. Both linear and branched polyethylenes have been used as the matrix and it is found that composites with the former can be processed to give the higher modulus. An important practical finding is that products with a Young's modulus well into the range shown by cortical bone can be produced. The critical step in the enhancement of the modulus is pressure annealing which alters the morphology of the linear polyethylene, encouraging the development of both crystallinity and crystallite size. The presence of butyl branches along the molecular backbone limits the extent to which these can be developed by pressure annealing and accounts for the failure of the process to improve the modulus of composites using the branched material. Comparison with similarly prepared samples of the pure polyethylenes shows that the development of orientation in the polyethylene is considerably restricted by the presence of hydroxyapatite particles, irrespective of whether pressure annealing is performed prior to extrusion. Consequently, the properties of these composites are less than might be expected from studies on the isolated polyethylenes.

Dedication: Professor Andrew Keller

I first met Andrew Keller in the early 50s when we were both working for ICI. At that time Andrew was researching in the Dyestuffs Division and associated with A F Wells and L B Morgan. I can still remember his fascination with unravellling the structure of polymer spherulites and the arguments stemming from Morgans's proposal that to explain the optical refractive index measurements, the polymer chains in spherulites must form helices. Polymer physicists are forever indebted that Andrew excited Charles Frank with this problem and that Warburton Hall then arranged for Andrew to become a Research Fellow at Bristol University, supported by the Ministry of Defence.

Andrew and I became close personal friends and after some years I eventually joined him at Bristol to set up a team on mechanical properties complementary to his team on polymer structure. It proved to be an exciting and enormously productive exercise. At that time (1965–70) Andrew's ideas on chain folding were reaching out into all aspects of polymer science and he and Charles Frank were an inspiration to all those at Bristol and increasingly to a world wide community of polymer scientists.

Andrew and I initiated the British Polymer Physics Group with Charles Frank as Chairman and maintained our close personal and professional contacts after I moved to Leeds. It was a great privilege to have known Andrew over nearly fifty years and to have been part of the tremendous developments in polymer science to which he contributed so greatly.

I. M. Ward

1. Introduction

Composites of polyethylene (PE) with hydroxyapatite (HA) are of considerable interest because of their

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potential medical application [1] as bone substitutes. To be successful in this role the composites need to fulfil two basic requirements; they should be biocompatible and mechanically equivalent to the bone they are replacing. The biocompatibility improves with increasing HA content [2] so a high content is favoured. The required mechanical properties depend on the particular application as natural bone displays a wide range of mechanical properties [3]. Thus, for low load-bearing applications, such as orbital floor reconstruction, the requirement is relatively modest and currently available composites, such as that marketed under the trade name HAPEX^{TM}, display an adequate Young's modulus and strength. These properties are not sufficient, however, to permit their use in high load bearing applications. Hydrostatic extrusion of HAPEX^{TM} improves the extensional modulus and strength [4, 5], although the modulus is still in the lower range of cortical bone.

Recent work [6, 7] on polyethylene has shown that the mechanical properties can be improved by the combination of pressure annealing in the vicinity of the hexagonal phase, to alter the morphology, and subsequent extrusion of this transformed morphology. Here, this processing route is applied to a range of PE/HA composites in an attempt to produce products with improved mechanical properties. In particular, the advantages of using, as the matrix, a polyethylene grade shown previously to be amenable to this processing combination, are assessed.

2. Experiment

2.1. Materials

Two grades of polyethylene, one branched (B) and the other linear (L), have been used as the matrix component of the composites. The branched grade ($\overline{M}_w \sim 225{,}000$ and $\overline{M}_n \sim 24{,}000$) is a copolymer formed from ethene and hexene and contains, on average, less than 1.5 butyl branches per 1000 carbon atoms. This grade is that used in the commercially available composite, HAPEX^{TM}. The linear grade has a higher molecular weight ($\overline{M}_w \sim 312{,}000$ and $\overline{M}_n \sim 33{,}000$) and was chosen because, in earlier work [7], it showed the greatest improvement in modulus when pressure annealed prior to extrusion. The filler is a calcium phosphate ceramic, hydroxyapatite (HA). Particles have a typical diameter of 7 to 10 μm.

Composites were made by compacting powdered blends of the two components after mixing in a Waring mixer. The mixture was compacted at 180°C under light pressure and the resulting billet was reground in a Fritsch pulveriser with a minimum sieve size of 0.2 mm. A second compaction, this time at 7 MPa, and a second regrind were performed before a final compaction to produce the starting billets. During the early stages of this process a fine white dust was observed, indicating that the final loading of HA in the composite is less than that intended. Table I lists the composites examined. Each is identified by a letter, B or L, indicating the grade of polyethylene chosen as the matrix followed by a number indicating the percentage by volume hydroxyapatite in the initial mix. The composite B40, containing a 40% volume fraction of HA in the branched grade of polyethylene, is marketed under the name HAPEX^{TM}and was compounded in a twin screw Betol melt extruder at QMW.

TABLE I Polyethylene/hydroxyapatite (PE/HA) composites

Composite	Matrix	vol% HA
B0	Branched PE	0
B40	Branched PE	40
L0	High MW Linear PE	0
L40	High MW Linear PE	40

2.2. Sample preparation

Cylindrical rods (diameter 7 mm) of material were subjected to high pressure annealing over a range of pressures in the vicinity of the hexagonal phase. The annealing temperature and time were fixed at 234°C and 1 hour respectively. In each annealing experiment two rods (one each of the unfilled and filled material) were joined together by fine steel wire and positioned in the pressure chamber. In this way, uncertainties in reproducing the annealing conditions, associated with annealing the rods separately, could be avoided and samples with identical annealing histories but differing in respect of their HA content could be prepared. After pressure annealing, samples were machined to a diameter of 5.1 mm and then extruded to a deformation ratio of 8 at 110°C through a 1.8 mm diameter die. For comparison, some samples were extruded without prior pressure annealing.

2.3. Differential scanning calorimetry

The melting behaviour of the PE matrix was examined using a Perkin Elmer differential scanning calorimeter, DSC7, at a heating rate of 10 K min^{-1}. The machine was calibrated using an indium standard. Crystallinity values were calculated from the area under the melting endotherm and using a value of 290 J g^{-1} for ΔH, the heat of fusion of the orthorhombic crystal. For composites a density of 3100 kg m^{-3} was assumed [8].

2.4. Mechanical measurements

Measurements of modulus and strength were performed in three point bend at room temperature. Span lengths of 130 mm and 50 mm were used for measurements of modulus and flexural strength, respectively. Dynamic mechanical measurements were also performed on some samples in three point bend, using equipment described previously [9]. The minimum test length was 60 mm which corresponds to an aspect ratio greater than 30 so that end effects should be small. Measurements were made for a peak to peak sinusoidal strain of 0.05%, at a dead load strain of 0.05% at temperatures between −150 and 70°C. (Strain is non-uniform throughout the sample in three point bend and this measure of strain corresponds to that at the surface halfway between the two supports, i.e. where the strain is a maximum.) The test temperature was controlled to an accuracy of ± 2°C by blowing nitrogen gas over a heater into the sample chamber. A freely oscillating torsional pendulum technique, of the type described by Heijboer *et al.* [10], was used to make measurements of the dynamic shear modulus. The rod-shaped samples were mounted vertically between two clamps, one of which was fixed. Torsional oscillations of the system were recorded by monitoring the rotation of the other clamp. The moment of inertia of the pendulum was chosen to give a resonant frequency close to 1 Hz. The shear modulus and loss factor were obtained, respectively, from the time period and logarithmic decrement of oscillations.

2.5. NMR measurements

NMR spectroscopy was used to investigate the crystalline orientation of the polyethylene component of the composites. Measurements were performed on a Varian crossed coil spectrometer operating at a proton resonance frequency of 60 MHz. Oriented samples were mounted in a slot drilled through a PTFE rod which acted as a carrier and could be rotated about its unique axis, thereby altering the angle between the draw direction of the sample and the direction of the magnetic field. The absorption signal, induced by sweeping the magnetic field through resonance (±25 G), was modulated at a frequency of 40 Hz and an amplitude of 0.1 G. The resulting derivative signal was amplified, filtered and smoothed before collection and subsequently integrated to yield the absorption line. Measurements were made at room temperature and angular steps in orientation of 10°.

Anisotropy of the second moment of the absorption line is used to investigate orientation within the sample. Measurements of this are perturbed by any broadening of the signal so, consequently, care needs to be taken to reduce artificial broadening to a minimum. For measurements here, broadening due to mean field drift during a scan and to signal smoothing were both less than 0.1 G. Broadening due to the finite amplitude of the modulation field [11] was also found to be negligible.

2.6. Electron microscopy

Two types of surfaces were prepared for transmission electron microscopy. Internal fracture surfaces were exposed by cleaving samples at liquid nitrogen temperature, while for etched surfaces, an interior surface was exposed by cutting with a glass knife in a Bright microtome at about −70°C. These cut surfaces were etched for 1 hr with a permanganic reagent consisting of a 1% solution of potassium permanganate in a 10 : 4 : 1 (by volume) mixture respectively of concentrated sulphuric acid, 85% orthophosphoric acid and water [12]. A standard two-stage procedure involving an intermediate cellulose acetate replica [13] yielded shadowed carbon replicas for TEM studies.

3. Results

3.1. Differential scanning calorimetry

An insight into the polyethylene morphology can be obtained from its melting behaviour. Results derived from the melting behaviour of filled and unfilled materials in the isotropic and extruded states are shown in Table II. The melting points refer to the positions of the prominent peaks.

3.2. Pre-extrusion morphology

3.2.1. Polyethylene (B0 and L0)

Figs 1 and 2 show the effect of different annealing pressures on the melting behaviour of the two polyethylene grades. For comparison, the unannealed branched polyethylene has a melting peak at about 130°C, which is slightly less than that observed in the linear grade. Pressure annealing produces a considerable increase in the melting temperature of both grades, although increasing the depth of the annealing (i.e. reducing the pressure) has a more significant impact on the linear grade, where the melting temperature rises to a value of about 142°C. In contrast, the melting temperature of the branched material is limited to about 139°C. Table II shows that the crystallinity is also increased by pressure annealing, and again, the magnitude of the change is greater in the linear grade.

TABLE II Characterisation of isotropic PE/HA composites

Ann Pres/ MPa	B0 0% HA		B40 40% HA		L0 0% HA		L40 40% HA	
	Melting point[a]	Crystallinity %	Melting point[a]	Crystallinity %	Melting point[a]	Crystallinity %	Melting point[a]	Crystallinity %
	Isotropic							
None	130.2	59.2	129.7	50.1	133.4	61.6	134.2	63.8
540	139.0	68.1	138.6	58.0				
520	138.8	64.2	138.1	57.5	140.8	89.8	141.3	97.9
500	139.6	63.2	139.4	56.5	140.1	89.4	140.8	96.9
480	140.8	58.9	137.6	45.1	142.4	91.9	142.0	93.2
	Extruded to draw ratio 8							
540	134 137.5	69.0	139.0	55.9	—	—	—	—
520	134.1 138	68.1	138.5	58.1	140.5	74.8	142.4	78.9
500	135.3 139.4	68.2	137.6	60.1	143.2	78.2	142.6	83.2
480	134 140.6	70.0	138.8	60.9	142.2	78.5	142.8	78.4

[a] The melting points refer to the positions of the prominent peaks/(°C).

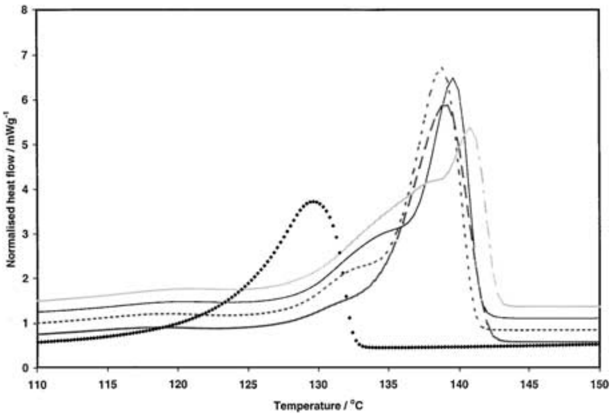

Figure 1 The melting behaviour of isotropic pressure annealed branched polyethylene (Grade HM4560). Samples have been annealed at 234°C for 1 hour at pressures; - - - - -, 540 MPa; – – – –, 520 MPa; - - - - - - - -, 500 MPa; - - - - - -, 480 MPa. Data for the unannealed sample, – –, is also shown.

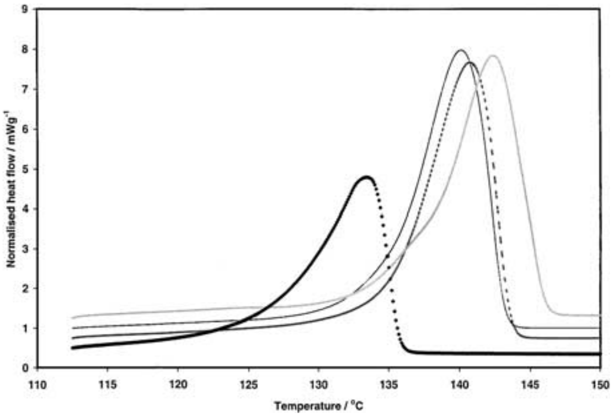

Figure 2 The melting behaviour of isotropic pressure annealed linear polyethylene (Grade HM5420). Key as for Fig. 1.

In linear polyethylene the higher melting temperature has been shown to be a direct result of the melting of thicker lamellae, with the melting point related to the lamellar size through the Gibbs–Thomson equation [14]. This equation predicts that lamellae of linear polyethylene with a thickness of about 80 nm would melt at about 139°C. Although differences in the surface free energy may need to be considered when applying the equation to branched polyethylene, it is reasonable to assume that the limitation to the increase in melting point of branched polyethylene is a consequence of limitations to the growth of the lamellae during pressure annealing. This probably arises because the chain branching restricts the ability of molecular sections to be accommodated within a crystallite when the stem length is greater than the distance between branches. For regular spacing along the molecular backbone, a branch content of 1.5 per 1000 carbons is equivalent to 1 branch every 86 nm. This restriction does not exist in the linear polyethylene so that the crystallite size develops further under the favourable thermodynamic conditions at lower annealing pressure.

Increasing the depth of the anneal also has a considerable impact on the shape of the melting curve, especially for the branched material. Fig. 1 shows that a pronounced shoulder develops on the low temperature side of the melting peak as the annealing pressure is reduced. A lower temperature melting peak at about 120°C also becomes more prominent. Both features have been observed in linear polyethylene subjected to pressure annealing, with their prominence, after annealing under specific conditions, depending on the molecular weight [15]. The shoulder is attributed to the melting of poor quality crystals formed by pressure crystallisation directly into the hexagonal phase during the return to ambient conditions at the end of the annealing process [16]. The low temperature peak is attributed to lower molecular weight material which has crystallised from the melt directly into the orthorhombic phase [17, 18]. The linear polyethylene investigated here has a high molecular weight which will help suppress both these effects. Furthermore, the presence of butyl groups in the branched grade may favour the conversion of more material to the melt during annealing and may enhance greater crystalline disorder upon subsequent crystallisation. This may explain why, after the initial rise in crystallinity the branched material shows a drop in crystallinity for greater depths of anneal.

3.2.2. PE/HA composites (B40 and L40)

The melting behaviours of the polyethylene matrix in pressure annealed composites with 40% HA are shown in Figs 3 and 4 for the branched and linear grades

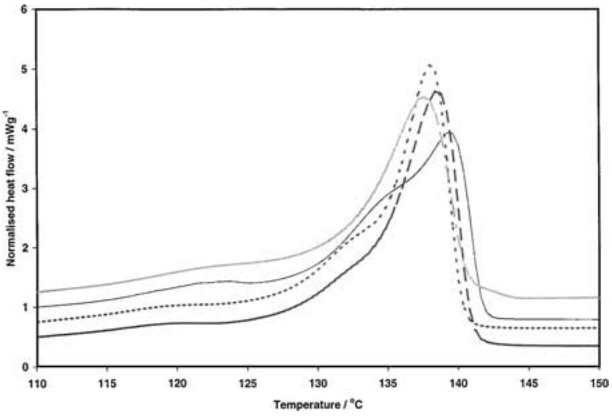

Figure 3 The melting behaviour of isotropic pressure annealed B40 composites. Key as for Fig. 1.

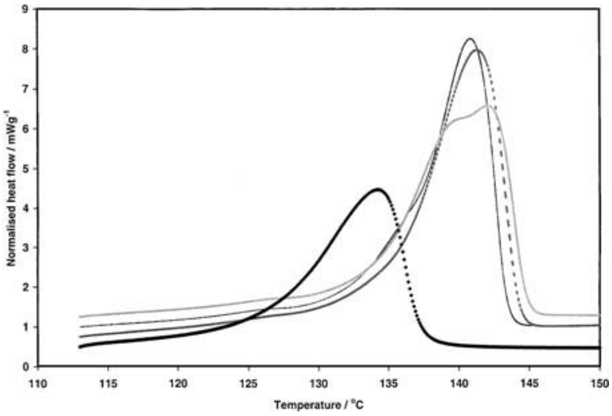

Figure 4 The melting behaviour of isotropic pressure annealed L40 composites. Key as for Fig. 1.

respectively. Results are presented for different annealing pressures and comparison with Figs 1 and 2 shows how the presence of hydroxyapatite affects the development of the polyethylene morphology. Generally, the melting behaviour of the branched PE in the B40 composite is similar to that of the unfilled material. The maximum melting point, achieved at low annealing pressures, is very similar, about 139°C, indicating that the development of lamellar size is again limited to about 80 nm. Changes in the shape of the melting curves are also similar to those seen in the unfilled material. It therefore appears, at least insofar as the DSC technique can probe, that the presence of the hydroxyapatite does not have a major effect on the development of the polyethylene morphology at the pressure annealing conditions considered here. This general conclusion also applies to the linear grade where incorporation of the filler has little effect on the melting behaviour of the polyethylene matrix until the annealing pressure is reduced to 480 MPa, when a low melting point shoulder becomes prominent. The melting point is also slightly lower than that of the equivalent unfilled material. These features may indicate the onset of limitations to the development of crystallite size, probably because of the small interparticulate separation associated with the high volume fraction of filler. The crystallinity values of the L40 composites are higher than those found in the unfilled material and are probably an overestimate owing to the loss of hydroxyapatite in the mixing and grinding stages of preparation.

3.3. Post-extrusion morphology

Generally, the effect of extrusion is to produce a small increase in the melting point and a smoother melting endotherm in the polyethylene. For the linear polyethylene this is true both with and without the HA filler. For the branched polyethylene, however, the unfilled extrudate shows two clear melting peaks, the second lower temperature melting peak appearing at a temperature of about 134°C, whereas the filled extrudate shows only one. This difference in behaviour is illustrated by the results for the samples annealed at 500 MPa, shown in Fig. 5. The presence of the filler therefore affects the morphology developed in the extrudate matrix based on the branched material, but for composites based on the linear polyethylene there is little evidence from DSC to suggest that the extrudate matrix is significantly affected by the presence of the HA. Finally, the crystallinity of the branched material is unchanged or increases slightly upon extrusion, while that of the linear material falls.

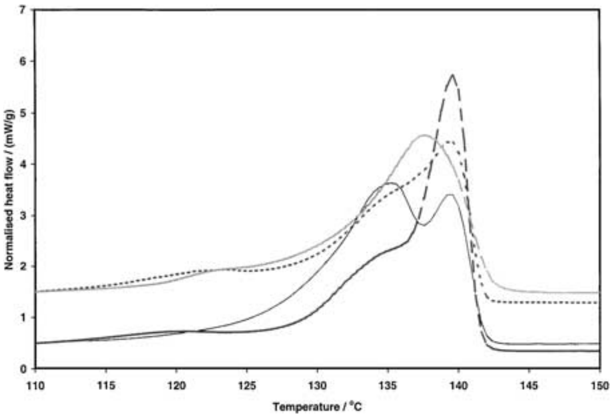

Figure 5 The melting behaviour of pressure annealed samples of B0; ——, isotropic, - - - - -, extruded to draw ratio 8; and B40; - - - - -, isotropic, - - - - - - - -, extruded to draw ratio 8. All samples have been annealed at 234°C and 500 MPa for 1 hour.

3.4. Mechanical behaviour

The results of testing samples in three point bend at room temperature are shown in Table III. As a reference, results for the unannealed but extruded composites show that incorporation of the HA filler in the branched PE raises the modulus from 2.3 GPa to 10.5 GPa. Similar results have been found when the linear PE is used as the matrix. Before considering whether the pressure annealing process is advantageous in improving the modulus of these composites it is appropriate to consider the effect of pressure annealing on the two polyethylenes by themselves.

The combination of pressure annealing the isolated polymer with subsequent extrusion to a standard deformation ratio produces a considerable enhancement in the modulus. The degree of improvement depends on the annealing conditions but is more substantial than that produced by simply incorporating the filler. For the branched material the increase is from 2.3 GPa to about 15 GPa, whereas the linear material shows a much larger increase to about 48 GPa. The strength of the branched material also shows a considerable improvement on pressure annealing.

When this combination is applied to the B40 and L40 composites two significant conclusions emerge.

TABLE III Mechanical properties of oriented PE/HA composites[a]

	B0 0% HA		B40 40% HA		L0 0% HA		L40 40% HA	
Ann Pres/ MPa	Modulus/ GPa	Strength/ MPa	Modulus/ GPa	Strength/ MPa	Modulus/ GPa	Strength/ MPa	Modulus/ GPa	Strength/ MPa
None	2.3	48	10.5	88	4			
540	11.3	92	11.5	79				
520	13.4	90	11.4	78	48	179	16	79
500	15.4	105	9.5	49	33	155	17.6	86
480	15.0	104	10.4	73	39	162	17	66

[a] All samples extruded to draw ratio 8 after pressure annealing treatment.

First, the modulus of the extruded pressure annealed L40 composites is typically about 17 GPa. This is the requirement if these materials are to be used in load bearing biomedical applications, and consequently this is an important practical finding. Secondly, oriented composites show a significantly lower modulus than the equivalent unfilled samples which have undergone the same annealing treatment. In the case of the branched grade, there is virtually no difference in the modulus of B40 whether pressure annealed or not before extrusion. The modulus is of the order of 10 GPa and the strength about 70 MPa. With the linear polyethylene as matrix, incorporation of the filler has led to a significant drop in the properties relative to what can be achieved by extrusion of the pressure annealed grade alone, in this case from about 40 to 17 GPa.

3.5. Dynamic mechanical behaviour

Fig. 6a shows the variation in the dynamic mechanical bending modulus with temperature for comparably processed filled and unfilled linear PE. These samples have been pressure annealed at 480 MPa prior to extrusion to a deformation ratio of 8. The modulus of the filled material is consistently less than that of the unfilled material over the whole temperature range and the results agree well with those obtained in static testing above. The loss behaviour of these materials (strictly, this is not the loss modulus but rather the variation in tan δ) as a function of temperature is shown in Fig. 6b. The curve for the unfilled material is typical of a linear polyethylene showing the low temperature γ relaxation at about -140°C and the high temperature α peak [19]. Between these there is a general background which is typically <0.01. The loss behaviour of the filled material is significantly different in one respect. Again, both the α and γ relaxations are present but the background loss between them is significantly higher than that seen in the unfilled material.

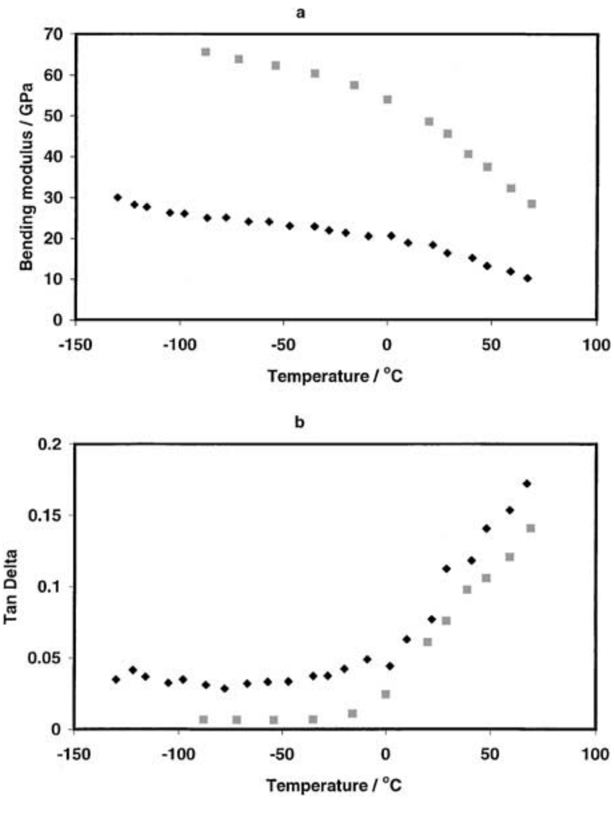

Figure 6 The dynamic mechanical behaviour of pressure annealed HA/PE composites using a linear polyethylene; ■, L0; ◆, L40. Samples have been annealed at 234°C and 480 MPa for 1 hour before extrusion to a draw ratio 8. a) bending modulus; b) relaxation spectra.

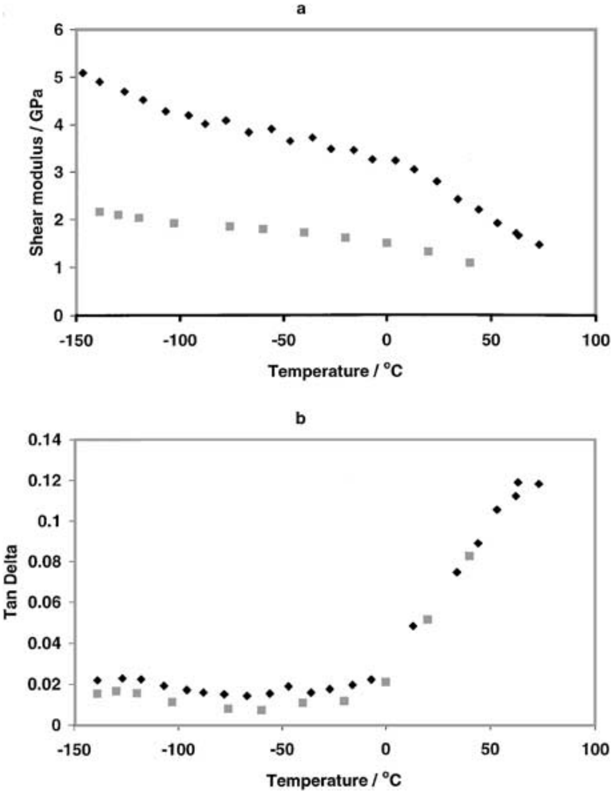

Figure 7 The dynamic mechanical behaviour of pressure annealed HA / PE composites using a linear polyethylene; ■, L0; ◆, L40. Samples have been annealed at 234°C and 480 MPa for 1 hour before extrusion to a draw ratio 8. a) shear modulus; b) relaxation spectra.

The results of dynamic torsional measurements on these samples are shown in Fig. 7. Unlike the situation in bending, the torsional modulus of the filled material is higher than that of the unfilled material across the temperature range. The loss behaviour (Fig. 7b), however, is similar to that seen in bending, in that there is a higher background loss between the α and γ relaxations in the filled material.

Fig. 8a shows the dynamic bending modulus as a function of temperature for a B40 composite which has been extruded to a deformation ratio of 8 but was not pressure annealed prior to extrusion. The loss behaviour for this sample as a function of temperature is shown in Fig. 8b. The results from Fig. 6, for the linear polyethylene composite, L40, pressure annealed before extrusion, are included for comparison. Fig. 8a illustrates the advantages that can be achieved by a suitable choice of polyethylene which is amenable to pressure annealing. The modulus of the oriented B40 composite is significantly less than that of the pressure annealed and extruded L40 sample across the temperature range investigated.

The peak at about -140°C in Fig. 8b is attributed to the γ relaxation and is believed to have the same

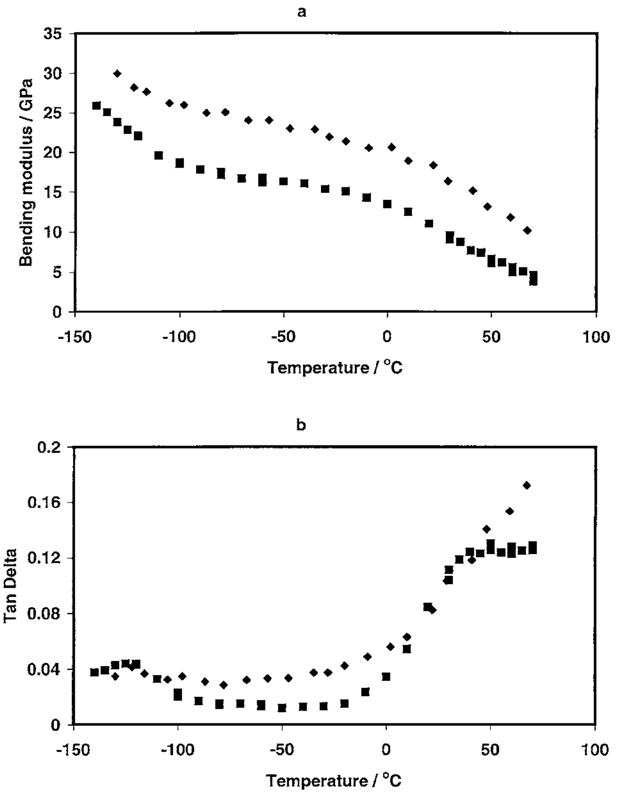

Figure 8 Comparison of dynamic bending behaviour of HA/PE composites extruded to draw ratio 8. ◆, L40, pressure annealed at 234°C and 480 MPa for 1 hour before extrusion and ■, B40, HAPEX^{TM}, no pressure treatment prior to extrusion. a) bending modulus; b) relaxation spectra.

molecular origin as the corresponding peak in the linear material [20]. The peak at about 40°C, however, is more complex than that seen in the linear material, and, although a β relaxation can be found in linear polyethylene [21], this is probably a predominantly α relaxation shifted to lower temperature by the smaller crystallite size of this unannealed branched PE [22]. Significantly, the loss behaviour between −80 and 0°C is considerably less in the B40 composite.

The results for the dynamic moduli in torsion and three point bend can be combined using a modified aggregate model [9] to gain some insight into the structure of these materials. For highly aligned aggregates of a basic structural unit these moduli are related through the equation

$$\frac{1}{E} = \frac{1}{E_u} + \frac{1}{G}\langle \sin^2 \theta \rangle \qquad (1)$$

where E_u is the extensional modulus of the basic unit and θ is the inclination of its unique axis to the sample draw direction. It has been shown earlier [7] that highly oriented pressure annealed linear polyethylene of medium to high molecular weight provides a good fit to this model. One of those materials is the linear polyethylene used here, and the data from the present work on L0, shown in Fig. 9, not surprisingly follows the model predictions. Fig. 9 also applies the model to composites of PE with 40 vol% HA, surprisingly with some success. The L40 sample has been pressure annealed at 480 MPa and 234°C for 1 hour prior to extrusion. The gradients of the straight lines through the L0 and L40 data give values for $\langle \sin^2 \theta \rangle$ of 0.018 and 0.15, respectively. These equate to Legendre second moment averages, $\langle P_2(\cos\theta) \rangle$, of 0.97 and 0.77. The fundamental conclusion from these data is that the basic structural units of the material are more highly oriented when there is no particulate filler present.

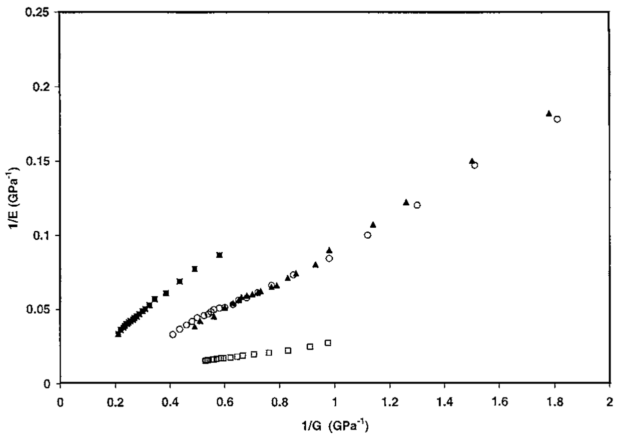

Figure 9 Aggregate model plots for oriented HA/PE composites: □ L0; ■, L40; O, B40, (samples pressure annealed at 234°C and 480 MPa for 1 hour before extrusion to a draw ratio 8) and ▲, B40, (sample extruded to a draw ratio of 8 without prior pressure annealing).

Finally, Fig. 9 also shows aggregate plots for B40 composites differing only in their initial morphology. The data share a common gradient, intermediate between those of the L0 and L40 samples, indicating that the orientation of the structural units is unaffected by the introduction of a pressure annealing stage prior to extrusion.

3.6. NMR

Fig. 10 shows typical proton resonance derivative curves (a) and the resulting absorption lines (b) for pressure annealed and oriented L0 and L40 samples. For these curves the magnetic field is inclined at about 45° to the draw direction. Both samples show a clear broad component but the L40 sample, and all other samples considered here, also show a prominent narrower component. Broad line NMR spectra are often separated into discrete components associated with the crystalline and non-crystalline regions [23], although a better fit can be produced when a third interphase contribution is introduced [24]. Here, the narrow component is too broad to be associated solely with mobile material and it is more probably associated with material showing restricted mobility. The broad component is, however, readily identified with the rigid crystalline regions and its relative contribution to the NMR signal is a measure of the crystallinity [25]. Clearly then, Fig. 10 shows that the presence of the HA particles restricts the development of crystallinity in the polyethylene matrix.

The anisotropy of the total second moment as a function of γ, the inclination between magnetic field and the sample draw direction, is shown in Fig. 11 for the two samples (L0 and L40) just considered. Clearly, the anisotropy in the second moment is greater in the unfilled sample suggesting that the orientation is greater.

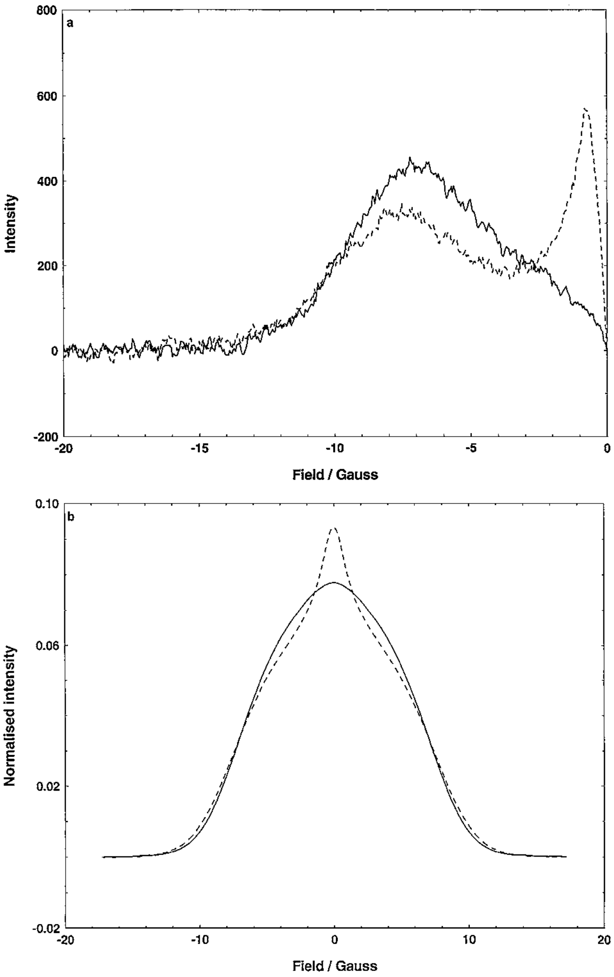

Figure 10 NMR curves for oriented pressure annealed samples using a linear polyethylene. Samples have been annealed at 234°C and 480 MPa for 1 hour before extrusion to a draw ratio 8. ——, L0; - - - - -, L40. a) derivative trace and b) absorption lines constructed from the derivative curves.

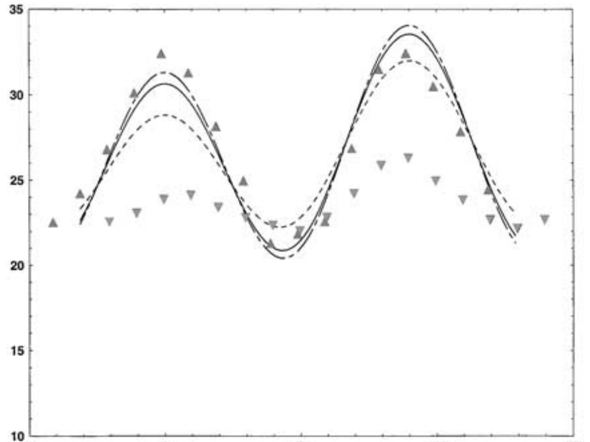

Figure 11 NMR second moment anisotropy in oriented samples of pressure annealed L0, ▲, and L40, ▼. Samples have been annealed at 234°C and 480 MPa for 1 hour before extrusion to a draw ratio 8. Lines represent fits to L0 data, ——, using parameters in Table IV; - - - - -, using $\langle P_2(\cos\theta)\rangle = 0.8$ and $\langle P_4(\cos\theta)\rangle = 0.66$; – – – – –, using $\langle P_2(\cos\theta)\rangle = \langle P_4(\cos\theta)\rangle = 1$.

Because of difficulties making an accurate separation of the narrow and broad components it was decided to obtain orientation information on the crystalline phase following the approach adopted in a previous publication [26]. The total second moment is written as the sum of the appropriately weighted individual components so that

$$\langle \Delta H^2 \rangle = \chi \langle \Delta H^2 \rangle_{crys} + (1-\chi)\langle \Delta H^2 \rangle_{amorph} \quad (2)$$

where χ is the crystallinity. The normalised second moment for the fully mobile material is negligible but for material with restricted mobility this may not be the case. If, however, the orientational dependence of this interphase contribution is small, as has been shown for a range of polyethylenes [27], it is reasonable to assume that $\langle \Delta H^2 \rangle_{amorph}$ is constant and that the observed anisotropy in the second moment originates from the orientational dependence of $\langle \Delta H^2 \rangle_{crys}$. McBrierty and Ward have shown that this, in turn, depends on the crystalline orientation and the NMR crystalline lattice sums that can be evaluated from a knowledge of the relative positions of protons within the crystal.

Using the calculated values for the lattice sums [27] Equation 2 can be expressed in terms of four unknowns, the crystallinity, χ, the normalised amorphous second moment, $\langle \Delta H^2 \rangle_{amorph}$, and the second and fourth moment averages, $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$, of the orientation distribution function for crystalline material within the sample. There are mathematical constraints on the possible values for $\langle P_4(\cos\theta)\rangle$ for any given value of $\langle P_2(\cos\theta)\rangle$ and it is thus necessary to impose some restrictions in the curve fitting. The results of preliminary curve fitting often yielded equal values for $\langle P_4(\cos\theta)\rangle$ and $\langle P_2(\cos\theta)\rangle$ and although this is mathematically possible it is not physically realistic. Previous work [28] has shown that crystalline deformation in extruded samples of the pressure annealed polyethylene follows the pseudo-affine deformation, so that $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ are not independent. Although the crystalline deformation in pressure annealed samples might not follow the pseudo-affine deformation scheme, the relation between $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ is close to that found in many cases, so it is considered reasonable to apply it here. It was also found necessary to constrain the values of the parameters χ and $\langle \Delta H^2 \rangle_{amorph}$ to ensure that the results from curve fitting were sensible. The crystallinity was assumed to be between 0.5 and 0.9 while $\langle \Delta H^2 \rangle_{amorph}$ was assumed to be less than 6 G^2. The results of curve fitting are given in Table IV. It is noticeable that $\langle \Delta H^2 \rangle_{amorph}$ is consistently found to settle at 6 G^2. The relaxation of the constrained range for this parameter led to values as high as 8 G^2 but the general conclusions are unaffected by this.

Fig. 11 considers the sensitivity and effectiveness of the curve fitting to the L0 data. The best fit (solid line) is obtained using values of 0.89 for χ and 0.95 for $\langle P_2(\cos\theta)\rangle$. The two dashed curves correspond to slightly different crystalline orientations. These curves indicate that the level of confidence that can be attached to $\langle P_2(\cos\theta)\rangle$ is limited to about 10 to 20%. They also show that the predicted second moment at an inclination of 90° to the static magnetic field is greater than that at 0°. This feature is not shown by the experimental data. It should be noted, however, that the predicted

TABLE IV NMR fitting parameters for oriented samples[a,b]

Sample	$\langle P_2(\cos\theta)\rangle$	$\langle P_4(\cos\theta)\rangle$	$\langle \Delta H^2\rangle_{\text{amorph}}/G^2$	% Crystallinity
B0	0.97	0.94	6	61
B40	0.66	0.46	6	68
PA L0	0.95	0.91	6	89
PA L40	0.50	0.27	6	77

[a] PA Pressure annealed at 234°C and 480 MPa for 1 hour.

[b] All samples oriented to draw ratio 8, but note samples based on the branched PE have not been pressure annealed prior to extrusion.

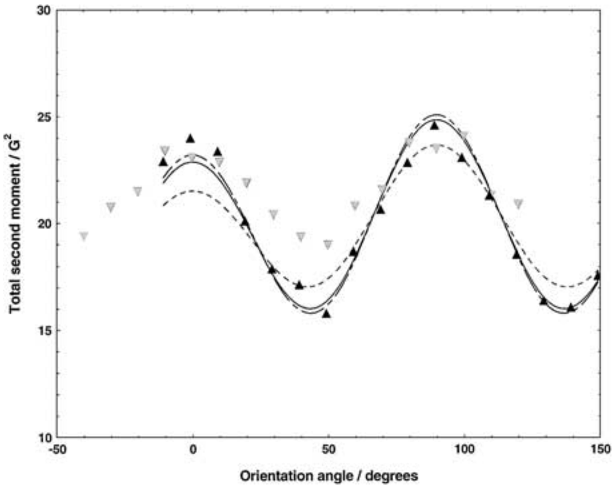

Figure 12 NMR second moment anisotropy in oriented samples of B0, ▲, and B40, ▼. Samples have been extruded to a draw ratio 8 without prior pressure annealing. Lines represent fits to B0 data, ——, using parameters in Table IV; - - - - - , using $\langle P_2(\cos\theta)\rangle = 0.8$ and $\langle P_4(\cos\theta)\rangle = 0.66$; - - - - -, using $\langle P_2(\cos\theta)\rangle = \langle P_4(\cos\theta)\rangle = 1$.

curves are based on the lattice sums calculated for the rigid component at very low temperature. The intrinsic crystalline second moment for the static field along the crystal axis would be expected to increase with temperature owing to greater interaction between the pendant hydrogen atoms on alternate backbone carbon atoms, arising from contraction of the chain. Ideally, measurements should be made at low temperatures to maximise the accuracy of the orientation results. Fig. 12 compares the second moment anisotropy in oriented B0 and B40 samples that have not been pressure annealed prior to extrusion. Again predicted variations in the second moment for the unfilled sample using different values for the orientation parameters show that the accuracy is limited.

Although the accuracy of measurements of orientation from NMR is limited, nevertheless, clear trends can be distinguished. Values for the orientation parameters, given in Table IV, clearly show a higher crystalline orientation in the unfilled samples than in the composites so that the presence of the HA particles obviously restricts the development of crystalline orientation. The data for the branched polyethylene show that it is not only limited to samples which have had their pre-extrusion morphology altered by pressure annealing. Measurements were also made on a sample of B40 that had been subjected to pressure annealing, (480 MPa) prior to extrusion. The orientation parameters for this sample agreed within experimental error with those found in the unannealed and oriented B40 sample.

Supporting evidence that the presence of HA restricts the development of orientation in the matrix comes from x-ray scattering studies of the B40 composite, extruded without prior annealing treatment. Azimuthal scans on the (002) reflection yield information on the crystalline orientation, although considerable absorption from the HA particles limits the accuracy of measurements. A value of 0.7 was found for $\langle P_2(\cos\theta)\rangle$ which agrees well with the value 0.66 found from NMR. By comparison, x-ray measurements on the unfilled material, subjected to an identical processing history, gives a value of 0.88 for $\langle P_2(\cos\theta)\rangle$.

Comparison with the findings from the aggregate model analysis shows good agreement in a number of respects. The most reliable results relate to the L0 sample which shows a value of 0.97 for $\langle P_2(\cos\theta)\rangle$, where the orientation relates to the structural units. The high crystallinity evident from DSC and NMR provides a firm foundation for identifying the crystallites with the structural units so that $\langle P_2(\cos\theta)\rangle$ may be expected to agree with the value found from NMR. For the other samples, there is less justification in identifying the structural units with the crystallites, but nevertheless, there is agreement on the relative degrees of orientation in these materials. Thus, both approaches show that the L40 sample has the lowest orientation (0.77 from aggregate analysis and 0.50 from NMR), and that the B40 composite shows a level of orientation intermediate between those of L0 and L40. Furthermore, the similar orientation in extruded B40 samples, regardless of the pre-extrusion treatment, is shown by both techniques.

3.7. Electron microscopy

The extruded materials without filler are highly oriented. Fig. 13a shows TEM of a fracture surface of the unfilled branched material, B0, pressure annealed at 480 MPa and extruded. The polyethylene structure is highly oriented, with a common orientation shared by the whole specimen. Fig. 13b shows the filled material (B40) after equivalent treatment. Here the orientation is disturbed with the “fibrillar” paths deviating, not only round the particles visible near the centre of the picture but also in the apparently clear areas to the left, where presumably there are particles lying above or below the fracture surface. This deviating orientation can be seen more clearly at higher magnification in Fig. 13c. The black dots are most likely tiny crystals of hydroxyapatite which have been carried off on the cellulose acetate used in the replication process.

Fig. 13d shows an etched surface of the unfilled branched material, B0. The texture as seen is much finer than that in Fig. 13a, since individual highly drawn lamellae are now distinguished. Large individual lamellae in high pressure crystallized specimens are known to survive the drawing process, albeit in a very highly sheared state [29]. The hydroxyapatite was found to interfere with the permanganic etching process, and so equivalent pictures are not available for the filled material.

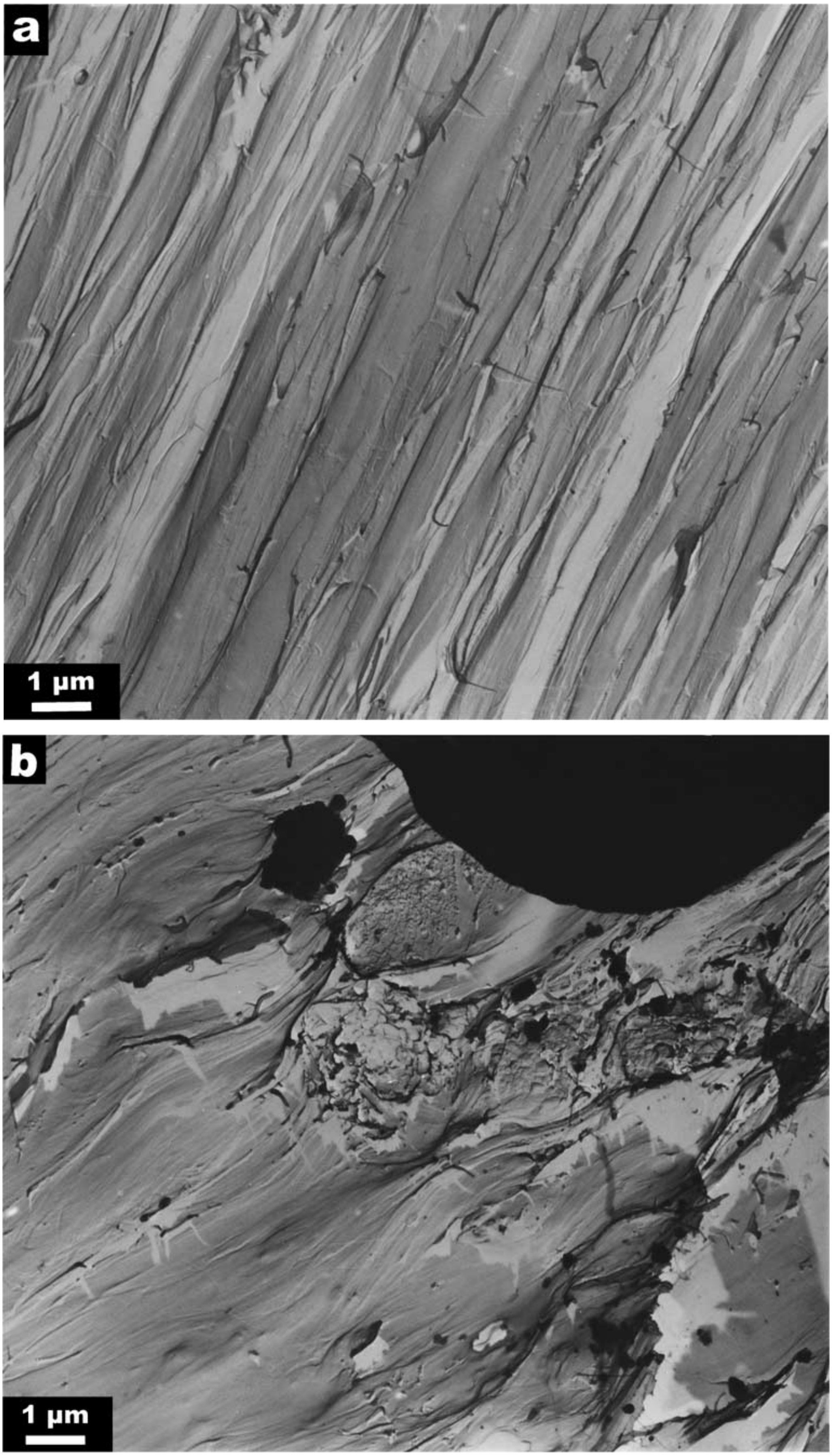

Figure 13 TEM micrographs of branched polyethylene (B0), (a) and (d), and the composite B40, (b) and (c). All samples were pressure annealed at 480 MPa and extruded to draw ratio 8. (a), (b) and (c) fracture surfaces; (d) etched surface. *(Continued.)*

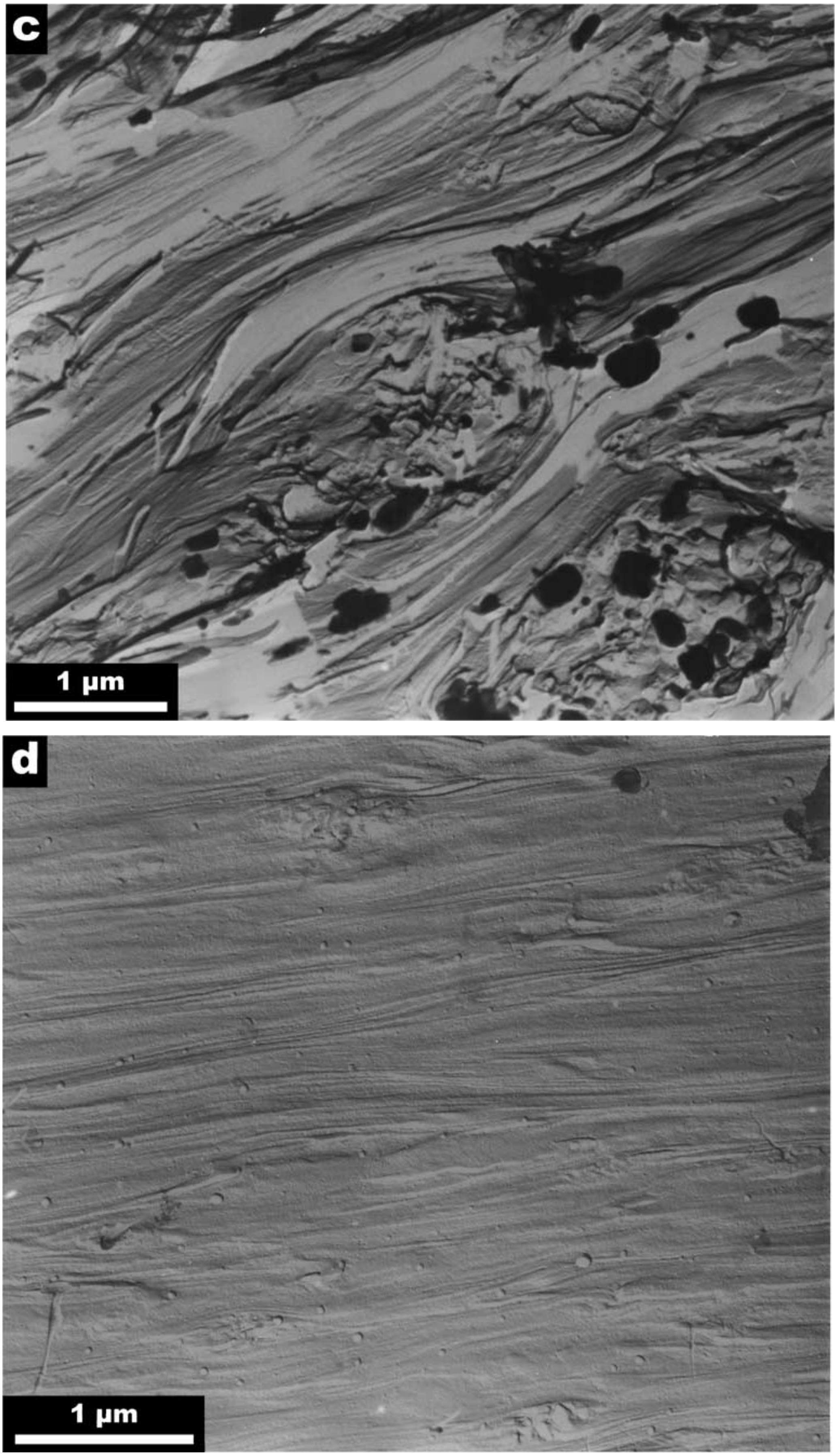

Figure 13 (*Continued.*)

4. Discussion

Altering the pre-extrusion morphology of the pure polyethylene clearly leads to an improvement in the mechanical behaviour of the extrudates. The degree of improvement, however, is considerably less for the branched grade than for the linear grade. This is probably attributable to the lower levels of crystallinity and crystallite size that can be produced by pressure annealing owing to the presence of butyl branches along the polyethylene backbone.

The incorporation of hydroxyapatite also results in an improvement in the extrudate mechanical properties when comparison is made solely between materials not subjected to pressure annealing. However, the combination of both steps, namely incorporation of HA and altering the pre-extrusion morphology, does not produce the expected benefits. Indeed, the mechanical properties (modulus and strength) of the filled material are significantly less than those of the unfilled material when both have been subjected to the same pre-extrusion annealing history.

Numerous models [30] relate the mechanical properties of a composite to those of its constituent components. At the simplest level, however, the incorporation of the stiff HA phase into the PE matrix would be expected to yield composites with a stiffness greater than that of the matrix, although the degree of improvement might depend on many factors. If it is assumed that the HA particles are homogeneous and possess a modulus greater than that of polyethylene, the fact that no improvement in the bending modulus is seen experimentally suggests that either the properties of the PE in the composite are not the same as those of the equivalently processed isolated polymer, or the bonding between the matrix and the filler is not perfect.

Considering the properties of the matrix first, it is clear that incorporation of hydroxyapatite has a significant effect on the orientation that is developed in the polyethylene matrix, irrespective of the starting morphology. In all cases, the evidence from NMR studies and, indirectly, from an aggregate model analysis of the mechanical behaviour, shows that the presence of the HA restricts the development of orientation. This conclusion is reinforced by microscopy showing clear orientational differences in the composites, although detailed investigations have been restricted by problems arising from the chemical interaction between HA and the etchants. Further evidence is provided by x-ray measurements. This restriction to the development of orientation in the matrix will have a detrimental effect on the mechanical properties and consequently limits the extent to which the composite properties can be enhanced. The presence of the HA in the linear polyethylene limits the crystallinity that can be developed by pressure annealing and this may affect the matrix properties, but this is likely to be secondary to orientation in its importance.

The suggestion that the critical factor determining the mechanical properties of the composites is molecular orientation is particularly reinforced by analysis of composites with the branched polyethylene. Oriented products of B40 possess different morphologies depending on their pre-extrusion treatment, yet the mechanical properties are very similar. These samples show very similar orientations in the aggregate model analysis and in NMR calculations of the crystalline orientation.

Although the restricted development of matrix orientation in the composites is probably the principal reason for the poorer than expected mechanical properties, it is also possible that a secondary effect results from imperfect bonding between the matrix and the filler. Evidence to this effect is obtained from measurements of the dynamic loss behaviour of Figs 6, 7 and 8. These curves indicate energy losses within the system for the particular cyclic mode of deformation, and are basically composed of peaks sitting on a general background. The peaks indicate energy losses occurring at specific temperatures and are attributed to the onset of molecular relaxations in response to the applied force. The background indicates the level of energy lost at all temperatures and arises from other energy dissipative processes such as, for example, friction. For composites this may arise from interactions between particles due to poor dispersion and from interactions between matrix and particle due to poor bonding. Figs 6, 7 and 8 show that the energy loss level between the two major relaxations varies considerably between samples.

Fig. 6b shows that the introduction of HA into the linear polyethylene leads to a much greater background loss in three point bending. The same result is seen in torsion (Fig. 7b) although the effect is smaller. It is significant that the loss is considerably greater in composites using the linear grade as can be seen from Fig. 8b. Electron microscopy indicates that the HA particles are relatively well dispersed in the branched polyethylene matrix, while those in the linear grade are poorly dispersed and tend to be clumped together. In the latter case, therefore, there may be considerable loss arising from interparticulate interactions and it is possible that a better dispersion would reduce the losses to levels seen in the B40 composites. In turn, this would be expected to raise the levels of modulus attainable with these composites. It is still possible, however, that other factors may restrict the improvement. Recent measurements [31] of Poisson's ratio on extruded B40 composites indicate that cavitation may be a problem and this may ultimately limit the effectiveness of processes such as pressure annealing.

Clearly then, the enhancement of modulus in extruded composites is dependent on many factors including orientation and morphology of the matrix and minimisation of loss processes. For the HA/PE composites considered here the most important criterion for enhancing the modulus is development of the crystalline orientation. This is restricted by the presence of the HA filler during the deformation process in all composites but, to some extent, the negative impact on mechanical properties can be counterbalanced, when using a linear polyethylene, by morphological changes produced prior to extrusion by pressure annealing. These morphological changes are quite important, not least because there is evidence that the orientation in composites with the linear grade is less than that in composites incorporating the branched material, yet the former have the larger modulus. It is also possible that the benefits of altering the morphology may be partially counterproductive in that they may lead to the poorer development of orientation during extrusion.

Finally, the detrimental effect of particulate presence on orientation and thereby mechanical properties has implications for composite modelling. Recent work [32] has calculated the properties of a composite of homogeneously dispersed spherical HA particles in an oriented PE matrix. The predicted properties, particularly the shear modulus, were found to be less than those determined experimentally and it was concluded that factors such as particle shape and dispersion also need to be considered. The modelling assumed that the PE matrix in the composite had the properties of an equivalently treated unfilled sample. The current work, however, shows that this assumption is incorrect so that the discrepancy between experiment and prediction is even larger and that therefore, presumably, such considerations have an even greater importance.

5. Conclusions

Processing, incorporating pressure annealing prior to extrusion, has been shown to be effective in improving some important mechanical properties of composites of HA with a linear PE. Composites which have a modulus of 17 GPa have been produced. This is well into the range required if these materials are to act as a bone substitute in load bearing applications. These advantages, however, are not realised in composites using a branched polyethylene, and are not as large as might be expected from measurements on the isolated polyethylenes. Several reasons for these limitations are proposed.

The dominant factor is the failure to develop adequate orientation in the polyethylene matrix of the deformed composite. To some extent, the use of pressure annealing to develop the crystallinity and crystallite size when using a linear polyethylene offsets the disadvantage of poorer orientation, so that composites with this grade can develop levels of modulus to satisfy engineering demands. Composites with the branched polyethylene do not benefit from pressure annealing prior to extrusion, because the levels of crystallinity and crystallite size that are developed are limited, presumably by the presence of branches along the molecular backbone.

For composites with the linear PE, the value of Young's modulus is also limited by the presence of significant loss processes in the system. These are observable in dynamic mechanical analysis and are not considered to arise from molecular relaxations. There is evidence of poor dispersion of the particles in the matrix, and it may well be that interaction between particles plays a significant role. It is concluded that better properties might be obtained by improving the particle dispersion.

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