JOURNAL OF MATERIALS SCIENCE **24** (1989) 2808–2814

In situ production of polyethylene fibres from polymer blends

F. EHTAIATKAR, M, J. FOLKES, S. C. STEADMAN
Department of Materials Technology, Brunel University, Kingston Lane, Uxbridge, Middlesex UB8 3PH, UK

The microstructure and mechanical properties of extruded specimens of a block copolymer–homopolymer polyethylene blend have been extensively studied. Through careful control of the blending and extrusion process, the dispersed polyethylene phase can develop, *in situ*, to yield stiff fibres having a tensile modulus of about 15 GPa. This fabrication strategy for composite materials is now being extended to the production of materials having ultra-high modulus polymeric fibres as well as those possessing novel combinations of physical properties.

1. Introduction

High-performance fibre-reinforced composites are now becoming important engineering materials in their own right and are penetrating into many market sectors previously dominated by metals. One barrier to their more widespread use is considered to be the often protracted fabrication times associated with combining the fibre reinforcement and matrix so as to give predictable properties in the final artefact. The use of short-fibre reinforced thermoplastics, which may be processed using extrusion and injection moulding technology, has brought about significant reductions in cycle times. However, difficulties still remain in terms of controlling the fibre length distribution and orientation in finished parts and coping with the increased viscosity of the melt due to the incorporation of the fibres.

One promising approach to circumvent some of these difficulties is to generate the fibres *in situ*, i.e. during the actual forming of the component. Providing care is taken during the forming process, it should, for example, be possible to produce fibres having a high modulus, in the range 20 to 100 GPa, and which will have comparable low strain mechanical properties with the more traditional reinforcements, e.g. glass or Kevlar.

In order to achieve this objective, it is necessary to bring together two very topical, yet disparate areas of research activity. The first concerns the study of the rheological properties and microstructure of extruded specimens of two-component blends. This has been the subject of extensive investigation over the last 10 to 20 years (see, for example, [1]) and it has been shown that under appropriate conditions, the dispersed phase can deform during processing to produce elongated structures, e.g. ellipsoids or even fibres. The microrheological interpretation of this has been reported by Han [2], McHugh [3] and Lyngaae-Jorgensen [4]. The corresponding studies using a block copolymer–homopolymer blend are far less numerous. However, Nandra *et al.* [5] have indicated that elongated structures can also be obtained in such a system. Indeed, there are good reasons to expect improved stabilization of the drawing process occurring in the dispersed phase owing to the surfactant nature of the copolymer; a feature which we have exploited in our own studies.

The second area of work of concern to us in the context of the present investigation is the production of ultra-high modulus fibres, especially those based on high-density polyethylene. A variety of novel techniques have been developed over the past 15 years or so, including uniaxial drawing [6], capillary extrusion [7], hydrostatic extrusion [8] and gel spinning methods [9]. It is the first of these approaches which will be of greatest interest to us in the production of *in situ* fibres. Indeed, many of the considerations important in the achievement of very high draw ratios, e.g. the control of molecular weight distribution, etc., are highly relevant to the present studies.

Accordingly, our objective was to establish the feasibility of producing stiff high-density polyethylene (PE) fibres within a matrix, by control of the drawing process occurring in the dispersed phase of the blend. For our studies, we chose a block copolymer matrix because it has a lower processing temperature compared with high-density PE and hence provides a temperature "window" within which we could optimize the conditions of extrusion. The copolymer also has a relatively high shear viscosity and hence significant stresses can be transferred from the matrix to the PE, thereby aiding the drawing process. The relevant aspects of the block copolymer used in our studies are included in the next section.

2. Experimental details

2.1. Materials

The materials used for the first part of the investigation were a Shell clear general purpose polystyrene (PS) and a block copolymer Shell Cariflex TR1102 (Kraton 102). The former was available in granular form and had a molecular weight, M_w of 2×10^4. The three-block copolymer consists of chains of the form

0022–2461/89 $03.00 + .12

polystyrene–polybutadiene–polystyrene (S–B–S). The molecular weight of the polystyrene (S) block is 10^4 and the polybutadiene (B) block 5.5×10^4, giving a volume fraction of polystyrene in the block copolymer of between 20 and 25%.

The structure and properties of this particular S–B–S copolymer have been extensively investigated over the past 10 to 20 years [10–12]. The microstructure of the copolymer consists of segregated phases of polystyrene within a matrix of the polybutadiene. The polystyrene exists in the form of long cylinders, having a typical diameter of about 15 nm. These cylinders can be very regularly arranged so as to form a macrolattice with spacings of the order of 30 to 40 nm. For the particular case of a cylindrical morphology, the lattice is hexagonal, although in most specimens this ordering is usually only short range. If very special care is taken, then melt-processed specimens can be fabricated such that most, if not all, of the material exhibits a uniformly oriented macrolattice or "single-crystal". Specimens such as this have been prepared using extrusion [13] and more recently by the use of a novel injection moulding process [14]. Indeed, the spacial ordering of the polystyrene phase can be such as to give discrete single-crystal low-angle X-ray patterns [15]. From the point of view of our present investigation, the morphology of the block copolymer has at least two important implications. As a matrix for our blend, the copolymer melt will be "structured" and this can lead to a high degree of molecular association between the matrix and added homopolymer. Also melt processing will result in some alignment of the polystyrene cylinders resulting in mechanical property enhancement in the extrusion direction. However, as we will see, this effect is very minor in comparison with the effect due to the added homopolymer.

The main part of the investigation has concerned the blending of the Shell Cariflex TR1102 (carrier phase) with a range of BP high-density polyethylenes (fibre forming phase). The grades of polyethylene investigated were: (a) Rigidex H020-54P ($M_w \sim 312\,000$); (b) Rigidex H060-45P ($M_w \sim 250\,000$); (c) Rigidex 9 ($M_w \sim 130\,000$); (d) Natene 60550AG ($M_w \sim 70\,000$); (e) Natene 60130AG ($M_w \sim 90\,000$).

2.2. S–B–S Copolymer–polystyrene blends

Earlier studies conducted in this laboratory concerned the effect of extrusion on the microstructure and properties of blends of the S–B–S block copolymer, Kraton 102, with homopolymer polystyrene [16]. The results obtained from this investigation are discussed again in this present paper because they form the basis for the development of our most recent work on S–B–S/PE blends.

The block copolymer and a general purpose grade of polystyrene were compounded using a two-roll mill. Three concentrations of polystyrene were used: 10%, 30% and 50% by weight. After granulation, the blend was extruded using a Reifenhauser single-screw extruder. The die used in these studies is shown schematically in Fig. 1. A significant feature of this die is the presence of a spider consisting of a simple plate containing 18 circular holes. Although this is commonly used as a means of removing the rotational memory of the melt in the screw, the melt will be subjected to elongational flow in its passage through each hole. It appears that this is important for the development of the particular microstructure to be described.

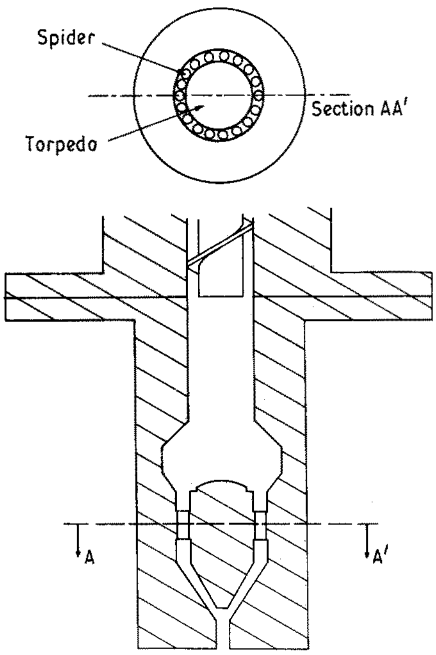

Figure 1 Diagram of the extrusion die used for the blend studies.

Fig. 2 shows a transverse section cut from the extrudate of the 30% PS blend. This is viewed in the optical microscope using transmitted light and reveals a two-phase structure on the scale of 1 μm. Confirmation of the fibrillar nature of the homopolymer PS comes from scanning electron microscopy (SEM). Transverse sections of the extrudate were etched with a strong oxidizing acid, known to attack the rubbery matrix. Fig. 3 shows the irregular break-up of the aligned structure. The fibrillar nature of the extrudate is also apparent from SEM observations of longitudinal fracture surfaces produced in three-point bending at low temperatures (Fig. 4).

The microstructure described above arises from a combination of two factors, namely a lowering of the surface energy of the dispersed homopolymer PS by the block copolymer and the formation of PS fibres by a process of elongational flow through the spider holes. It is interesting to note that the formation of this microstructure depends on a delicate balance of these factors, e.g. alterations to the volume fraction of homopolymer PS have a marked effect on the blend microstructure; for 10% PS, the blend shows no evidence of fibre formation, whereas for 50% PS almost perfect fibres are produced, as shown in Fig. 5. If swollen in a selective agent for the polybutadiene phase of the S–B–S copolymer, the dimensions of the blends changed in an anisotropic way, there being virtually no change parallel to the homopolymer PS fibrils and with all of the swelling occurring laterally [16]. The mechanical properties of the blends are also compatible with the presence of long continuous fibres of homopolymer PS embedded in the S–B–S matrix. For further details, the reader is referred to Arridge and Folkes [17].

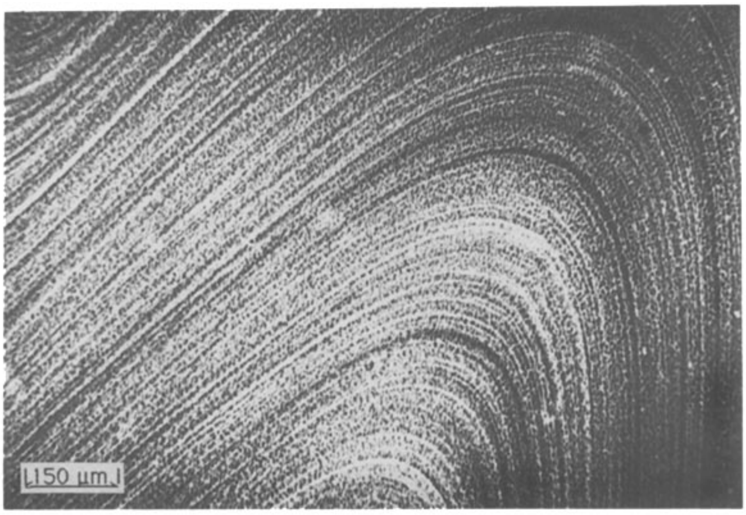

Figure 2 Optical micrograph of a transverse section cut from a blend of the block copolymer Cariflex 1102 with 30% homopolymer polystyrene, showing the existence of a striated two-phase structure.

Overall, the microstructure and physical properties of these blends confirm the feasibility of producing fibre-reinforced composite materials by the controlled extrusion of incompatible or partially incompatible blends. In these studies, the homopolymer PS fibres were formed, rather unexpectedly, by flow through the die assembly. Nevertheless, the principle has been established in this work and has enabled us to develop a specific methodology for the fabrication of S–B–S/PE blends in which the PE has a high stiffness. This work will now be discussed.

2.3. Self-Reinforcing S–B–S/polyethylene blends

2.3.1. Formulation and compounding of blends

The polyethylene grades described in Section 2.1 were blended in 40/60 wt % and 20/80 wt % ratios with the Shell Cariflex material, respectively. The appropriate blends were initially mixed using a ribbon-blade mixer. The blends were then compounded using a Gay's TS40-DVL twin-screw compounding extruder fitted with a die consisting of a simple plate containing six holes. The barrel temperature varied from 135° C at the feed hopper to 180° C at the die. Blends containing the 60550AG material in powder form were also prepared by cryogenically grinding the polyethylene to a particle size of approximately 400 μm. No significant change in molecular weight resulted from this.

2.3.2. Ram extrusion

The blends were granulated and, using a capillary rheometer, were then extruded at temperatures slightly above (+ 1° C) the melting point of the dispersed polyethylene phases. Extrusion at these temperatures (e.g. 130° C) was possible because the S–B–S phase existed as a melt above about 90° C and therefore acted as a carrier for the polyethylene particles.

Two rheometers were used during the work. A Davenport capillary rheometer was used to investigate the effect of fibre-forming ability of the individual polyethylene grades and its relation to die geometry. The ability of the polyethylene particles to form fibres was related to molecular weight and residence time available to untangle the polymer chains. It has also been found by Porter *et al.* [7] that higher pressures (approx. 25 000 p.s.i., $\sim 172.25\,\mathrm{N\,mm^{-2}}$) promote orientation induced crystallization and the formation of chain-extended structures in polyethylene. An

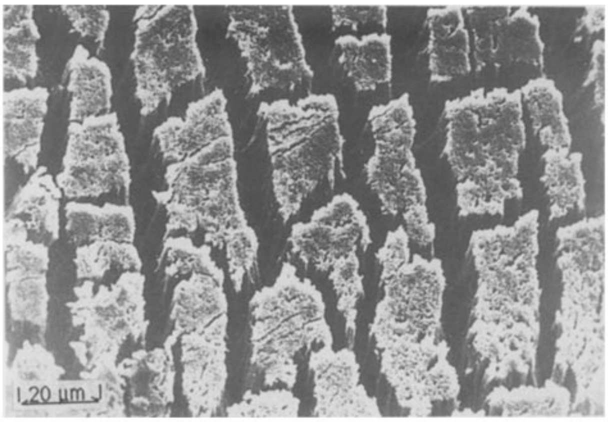

Figure 3 Etched transverse fracture surface for the blend of Cariflex 1102 with 30% homopolymer polystyrene.

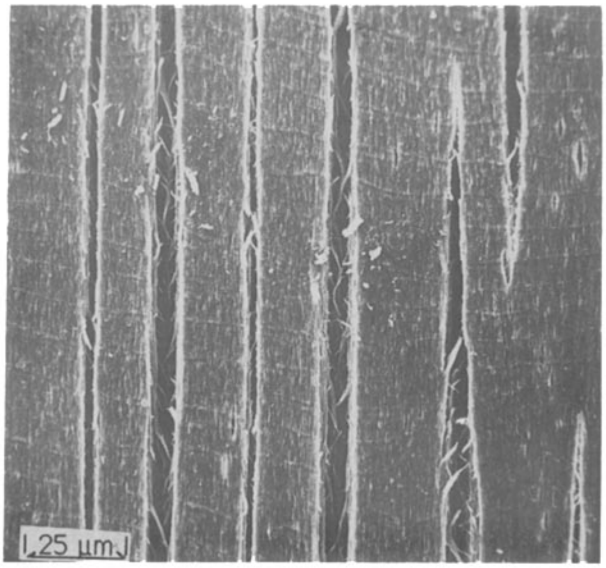

Figure 4 Etched longitudinal fracture surface for the blend of Cariflex 1102 with 30% homopolymer polystyrene.

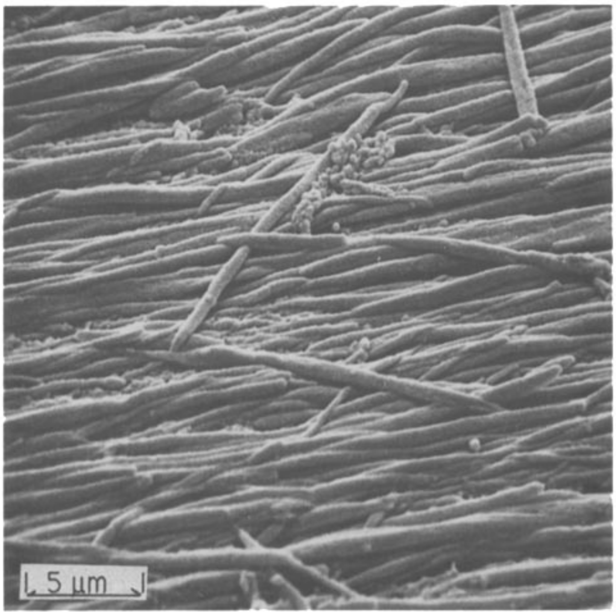

Figure 5 Scanning electron micrograph of an etched longitudinal section cut from a blend of Cariflex 1102 with 50% homopolymer polystyrene, following the processes of milling and screw extrusion.

analysis of the effect of pressure on the polymer blends was therefore conducted using an Instron capillary rheometer capable of die entrance pressures in excess of 25 000 p.s.i.

2.3.3. Structural examination of the blends

It will be shown that as a result of the particular choice of compounding route chosen, together with the elastomeric nature of the S–B–S block copolymer, a single investigative technique could not reveal all the structural detail necessary. Accordingly, a range of techniques was used including optical microscopy, scanning electron microscopy and differential scanning calorimetry.

2.3.3.1. Optical microscopy. Initial examination of the blends was carried out using transmission light microscopy. For this, thin sections of approximately 10 μm were cut parallel to the extrusion direction using a sledge microtome. Sections were examined using a Reichert Jung Microstar fitted with crossed polarizers.

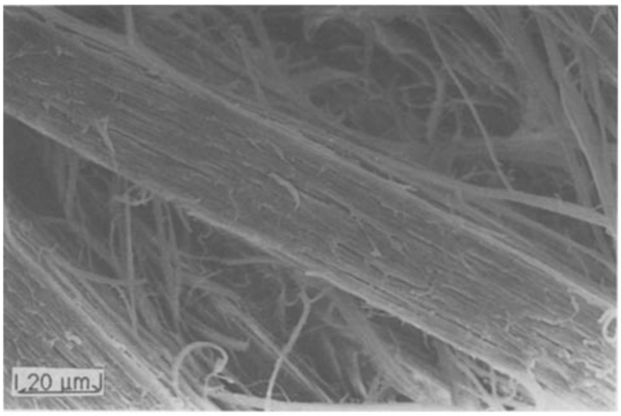

Figure 7 Etched section of sample in Fig. 6 where S–B–S phase has been selectively removed.

2.3.3.2. Scanning electron microscopy. In order to derive information concerning the structure of the blends using this method, it was necessary for the samples to be treated to give some form of topographic relief. Microtomed sections were therefore etched using an etch similar to that used by Folkes and Reip [16] and used for examining the structure of rubber-toughened polymers [18]. It consists basically of chromic and phosphoric acids, which give a powerful oxidizing etch which preferentially attacks unsaturated rubber. After coating the samples with gold/palladium, the examination of the structure was carried out using a Stereoscan 600 scanning electron microscope.

2.3.3.3. Differential scanning calorimetry. DSC traces for the blends were obtained using a Perkin Elmer DSC-2 differential scanning calorimeter. Samples of approximately 5 mg were scanned at a rate of 20 deg min^{-1}. The technique was used to show the existence of any chain-extended structures by the presence of multiple melting endotherms.

2.3.4. Results

Light microscopy of the appropriate blends indicated that polyethylene fibres had only formed in those polyethylene grades of molecular weight < 130 000. This was probably due to the short residence times

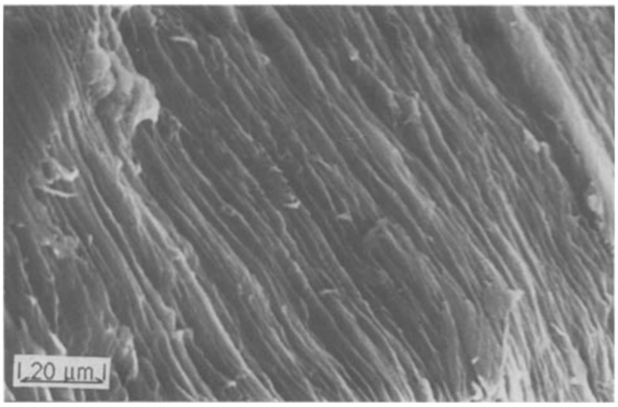

Figure 6 Longitudinal section of the 60/40 S–B–S/60550AG blend parallel to the extrusion direction.

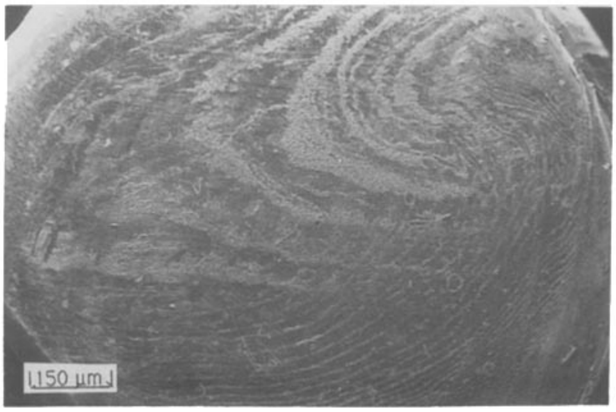

Figure 8 Scanning electron micrograph of an etched transverse section of the 60/40 S–B–S/60550AG blend. After twin-screw extrusion.

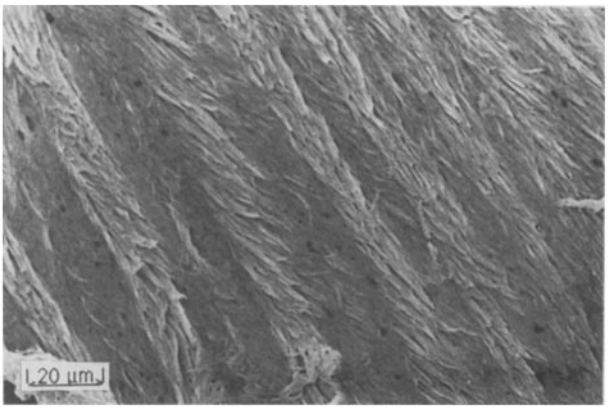

Figure 9 As Fig. 8 but at a higher magnification showing a striated polyethylene phase within the S–B–S.

available in the die to untangle the polymer chains in the high molecular weight materials.

Natene 60550AG and Natene 60130AG were both found to have formed fibres using a range of capillary dies in the Davenport rheometer. However, an examination of the microstructure of these samples prior to ram extrusion, i.e. after twin-screw extrusion, indicated that the polyethylene already existed as discrete fibres. Fig. 6 shows an SEM section of the 60/40 S–B–S/60550AG blend parallel to the extrusion direction. This indicates that an oriented structure exists. Etching to selectively remove the S–B–S phase in Fig. 7 indicates the presence of PE fibres, although not all the S–B–S has been removed in this micrograph. The fact that the PE fibres form so easily is very significant because the fibres were formed using a conventional twin-screw extrusion operation where no special die requirements had been utilized. One explanation for this may be the lowering of the surface energy of the dispersed homopolymer polyethylene by the block copolymer. The latter aids the formation of the fine fibrils by elongational or stretching flows, which may be present within the extruder barrel e.g. over the screw flights.

Fig. 8 shows a scanning electron micrograph of an etched transverse section of the above blend. This indicates that the initial dispersion of the polyethylene was rather poor and closer inspection (Fig. 9) shows the polyethylene fibres exist as a striated structure within the S–B–S matrix.

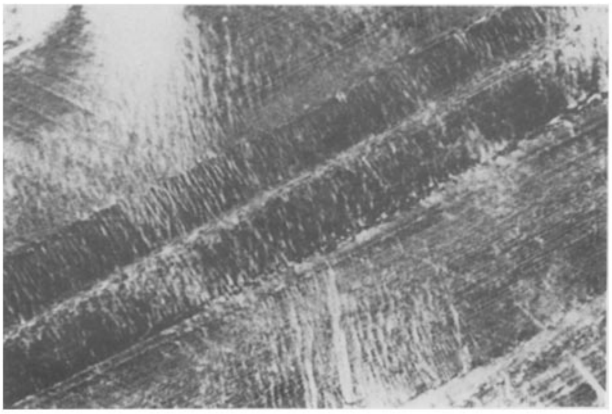

Figure 10 Optical micrograph under crossed polarizers of the capillary extruded 60/40 blend.

Application of a tensile stress to the screw extruded 60550AG and 60130AG based blends indicated that the samples formed a neck. Cold drawing of the 40 wt % polyethylene samples resulted in a markedly stiffer product. The natural draw ratio of these samples was about 10:1. Modulus measurements were conducted on the 40 wt % polyethylene blends in both the as-extruded and cold-drawn conditions. In the case of the cold-drawn samples the thread-like nature of the material led to slippage of the samples in the tensometer grips, producing a lower modulus value than expected. This was overcome using a dead-load type experiment whereby weights were progressively added and a cathetometer was used to measure the extension between two marks on the sample. Using this method, and by applying a simple rule of mixtures formula to the composites, the moduli of the polyethylene in the cold-drawn 60550AG and 60130AG blends was found as 10 and 8.5 GPa, respectively. The following formula, derived from the rule of mixtures, was used to estimate the modulus of the PE fibres

$$E(\mathrm{PE}) = \frac{E(\mathrm{composite})}{v} - \frac{E(\mathrm{matrix})(1 - v)}{v}$$

where v is the volume fraction of PE. Measurements on the screw-extruded samples indicated a modulus of about 2.0 GPa for the polyethylene fibres, indicating little orientation within the fibrous phase prior to cold drawing. This is hardly surprising, however, because no control was exercised over the conditions required to produce a high degree of orientation.

Ram extrusion of the 60/40 S–B–S/60550AG blend (hereafter simply referred to as the 60/40 blend), through a die of $L{:}D$ ratio 2.4:1 and at a pressure of 2500 p.s.i. ($\sim 17.23\,\mathrm{N\,mm^{-2}}$) resulted in a fairly stiff product which could not be cold drawn. Fig. 10 shows a micrograph of the blend indicating that a definite core region exists in the centre of the sample which is most likely related to the extensional flow field close to the axis of the capillary. Closer inspection has shown that a "shish-kebab" morphology is apparent in the core region and differential scanning calorimeter (DSC) traces showed a double melting peak confirming the existence of this chain-extended material. Ram extrusion of the 60/40 blend at higher pressures, obtained using a longer die (e.g. $L{:}D$ ratio 69:1) has resulted in a spreading of the core region across the width of the sample.

DSC traces for blends extruded through a range of pressures (2500 to 27 500 p.s.i., ~ 17.23 to $189.5\,\mathrm{N\,mm^{-2}}$) revealed either double or single melting peaks. These, and the modulus results are summarized in Table I. Results indicate that the most successful blend was achieved by ram extrusion of the 60/40 blend at 131° C at a pressure of 4160 p.s.i. ($\sim 28.66\,\mathrm{N\,mm^{-2}}$). This blend possessed polyethylene fibres with a melting point of 412.4 K (see Fig. 11) which was comparable to the increase in melting point achieved in other studies on high modulus polyethylene fibres by Capaccio and Ward [19]. Further, wide-angle X-ray diffraction

TABLE I Summary of results obtained for 60/40 S–B–S/60550 AG blend. Melt-crystallized melting temperature 400 K.

Sample	Die entrance pressure (p.s.i.)*	L/D ratio	DSC melting peak		PE modulus (GPa)
			Peak 1 (K)	Peak 2 (K)	
As-extruded 60/40 blend	–	–	400.5	–	2.0
Cold-drawn 60/40 blend	–	–	404.0	–	10.0
Capillary extruded 60/40 blend	5542	2.4	–	410.1	6.0
	5849	8.8	–	408.6	2.0
	4163	12.2	–	412.4	12.0
	8064	25.0	404.0	412.1	10.0
	12 904	40.8	408.0	410.9	5.0
	28 230	69.0	404.0	410.1	5.0
Capillary extruded 60/40 blend (P.E. Powder)	9010	25.0	–	412.0	13.0
Capaccio and Ward [19]	–	–	–	412.4	30.0

Data given for maximum modulus achieved per sample.
*10^3 p.s.i. ≡ 6.89 N mm^{-2}.

patterns for this blend indicate an oriented product exists (Fig. 12). The diffraction pattern shows some degree of disorder indicating that not all of the PE is well oriented at this stage. Also an amorphous halo is apparent due to the presence of the S–B–S matrix phase. Modulus measurements, however, have resulted in a lower modulus than was first expected, based on the DSC results. Scanning electron micrographs show the reason for this was probably due to phase separation of the two phases during extrusion through the capillary die. Fig. 13 clearly shows a region of densely packed polyethylene fibres alongside a depleted zone, resulting in a structure consisting of a polyethylene core surrounded by an elastic S–B–S sheath. The PE fibres in the core region are more clearly shown in the etched transverse section in Fig. 14. We feel that the high degree of phase separation may occur either in the rheometer barrel or the die, with the former case more likely. Irrespective of the location of this migration, it is probably caused by the large viscosity ratio of the two phases and by the significant normal stresses developed in the block copolymer matrix.

An increase in modulus of about 1 GPa has been achieved by the use of 60550AG powder in place of granules. This was probably a result of the fact that it was easier to elongate the smaller powder particles than the large agglomerates. However, SEM studies indicate that the use of powder has not eliminated the phase separation problem. Work is currently in progress to minimize its effect as it is felt that this will greatly improve the moduli of the composites. However, it is very likely that we are considerably underestimating the stiffness of the polyethylene fibres in our blends; this value is derived indirectly from the blend modulus and the application of the rule of mixtures, which is only applicable to fibres having large aspect ratios.

3. Concluding remarks

The microstructure of extruded specimens of block

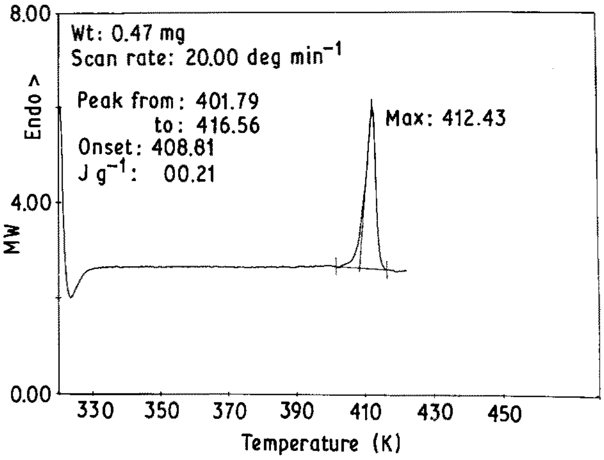

Figure 11 Differential scanning calorimeter trace of the 60/40 blend.

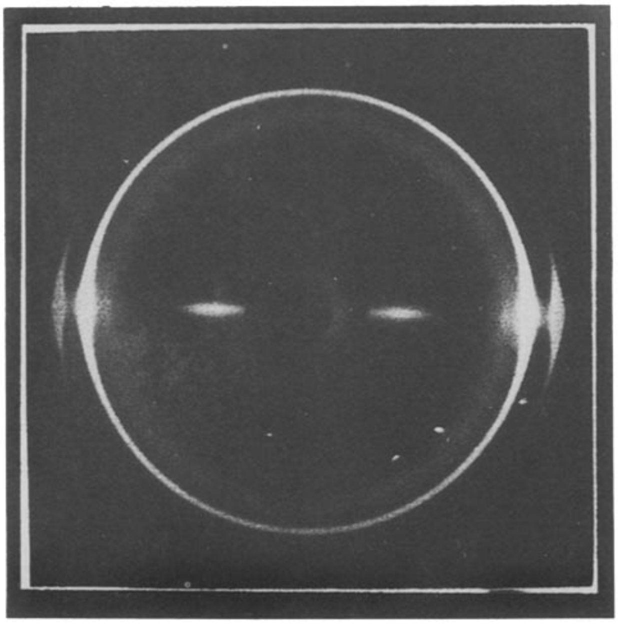

Figure 12 Wide-angle X-ray diffraction pattern for the 60/40 blend.

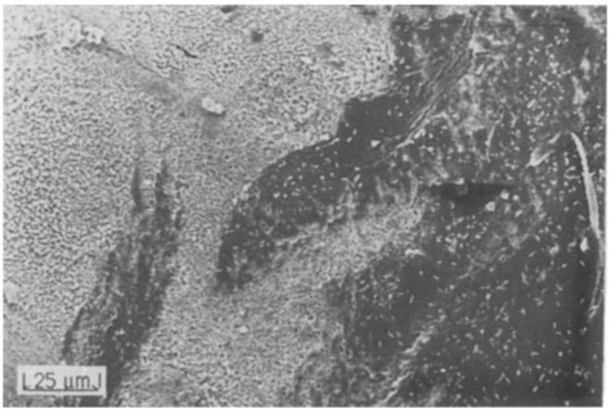

Figure 13 Transverse SEM section of 60/40 blend after capillary extrusion. The micrograph clearly shows a region of densely packed polyethylene fibres in the core alongside a depleted zone in the sheath.

copolymer–homopolymer polyethylene blends has been studied using light microscopy and scanning electron microscopy. By careful control of the blending process and subsequent extrusion, it was found that the dispersed polyethylene formed well-developed fibres aligned parallel to the extrusion direction. These fibres are produced primarily as a result of the elongational flow field pertaining at the die entrance and by a lowering of the surface energy of the polyethylene by the block copolymer matrix.

The low-strain mechanical properties of the blends have been characterized for loads applied parallel to the fibre axis. The tensile moduli obtained indicated that we are currently achieving a modulus for the polyethylene of about 15 GPa, i.e. comparable to that exhibited by many commercially available polymeric fibres. However, this figure is derived from the blend modulus using a simple rule of mixtures calculation. Because at the present time we have no information concerning the effective aspect ratio for the polyethylene fibres, it is most likely that we are grossly underestimating the true stiffness of the fibres. Indeed, the DSC results suggest that the fibres have a high proportion of chain-extended material and as such their moduli should be well above the derived figure of 15 GPa. Through optimization of the die geometry and carefully controlling the rheological properties of the blend so as to produce specimens with improved dispersion of the polyethylene, more effective utilization of the fibre reinforcement is anticipated.

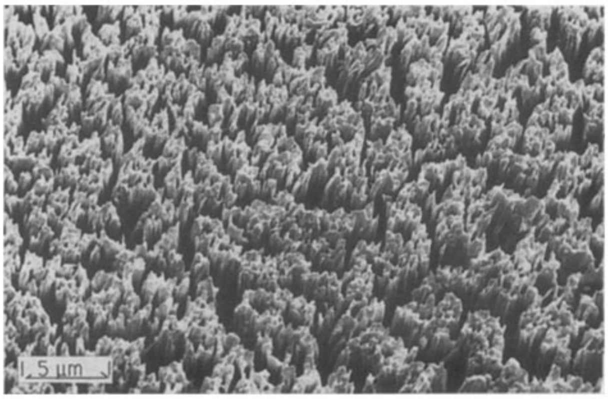

Figure 14 As Fig. 13 but at a higher magnification clearly showing the PE fibres in the core region.

Overall, the work has provided a clear indication of the feasibility of producing stiff fibres, *in situ*, by the controlled extrusion of a blend. This provides a basis for the development of a wide range of innovative composite materials, while at the same time avoiding many of the inherent difficulties associated with the processing of more traditional fibre-reinforced thermoplastics.

Acknowledgements

We thank Shell Chemicals UK Ltd for the supply of the block copolymer used in these studies. We are very grateful for the provision of an SERC Research Studentship for SCS. Finally, our thanks to Mr I. Drinkwater and Dr W. Gray for their invaluable contributions during the course of this programme work.

References

1. D. R. PAUL and S. NEWMAN, "Polymer Blends", Vols 1 and 2 (Academic, New York, 1978).
2. C. D. HAN, "Multiphase Flow in Polymer Processing" (Academic, New York, 1981).
3. A. J. McHUGH, *J. Appl. Polym. Sci.* **19** (1975) 125.
4. J. LYNGAAE-JORGENSEN, in "Processing, Structure and Properties of Block Copolymers", edited by M. J. Folkes (Applied Science, London, 1985) Ch. 3.
5. D. S. NANDRA, D. A. HEMSLEY and A. W. BIRLEY, *Plast. Rubber Mater. Appl.* February (1979) 38.
6. G. CAPACCIO and I. M. WARD, *Nature Phys. Sci.* **243** (1973) 143.
7. R. S. PORTER and N. E. WEEKS, *J. Polym. Sci. Polym. Phys. Edn* **12** (1974) 635.
8. I. M. WARD, *J. Mater. Sci.* **9** (1974) 1193.
9. P. J. LEMSTRA and P. SMITH, *ibid.* **15** (1980) 505.
10. M. J. FOLKES and A. KELLER, in "Physics of Glassy Polymers", edited by R. N. Haward (Applied Science, London, 1973).
11. E. FISCHER, *J. Macromol. Sci. Chem.* **A2** (1968) 1285.
12. A. KELLER, E. PEDEMONTE and F. M. WILLMOUTH, *Nature* **255** (1970) 538.
13. M. J. FOLKES, A. KELLER and F. P. SCALISI, *Kolloid Z.Z. Polym.* **1** (1973) 251.
14. P. ALLEN, F. EHTAIATKAR and M. J. FOLKES, to be published.
15. A. KELLER, E. PEDEMONTE and F. M. WILLMOUTH, *Kolloid Z.Z. Polym.* **238** (1970) 385.
16. M. J. FOLKES and P. W. REIP, *Polymer* **27** (1986) 382.
17. R. G. C. ARRIDGE and M. J. FOLKES, in "Processing, Structure and Properties of Block Copolymers", edited by M. J. Folkes (Elsevier Applied Science, London, 1985) Ch. 4.
18. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977).
19. G. CAPACCIO and I. M. WARD, *Polymer* **15** (1974) 233.

Received 19 January
and accepted 13 February 1989