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Polyethylene–polyethylene microfibrillar composites

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Solid-state drawing of melt-crystallized, or gel(solution)-crystallized, polyethylene (PE) is well established as a means of producing high modulus high-strength fibres. Here, an alternative route, based on melt-processing, is reviewed and its merits are assessed. Contrary to expectation, melt processing of flexible chain polymers can directly yield oriented products with good mechanical properties, without the need for post-drawing in the solid state. The melt-processed PE can give a special microfibrillar composite morphology which results in good mechanical properties. The paper also reviews aspects of composites design by comparing these microfibrillar composites with traditional fibre composites and molecular composites.

1. Introduction

This paper is part review and part update on some previous work on producing high-performance polyethylene (PE) through a melt-processing route [1–4].

Solid-state drawing of spherulitic polyethylene to produce high-modulus fibers was investigated by Ward and co-workers [5,6], and there is now a commercial product based on this. Typical moduli and strength are 70 and 1.5 GPa, respectively. Solution-state "gel-spinning" technology is another commercial process [7] for making high-modulus high-strength PE fibers. In laboratory gel-spun fibres, moduli of 155 GPa and strengths as high as 6.4 GPa have been reported [8].

An alternative method is to produce high-modulus PE by melt processing [1–4], as opposed to solid-state, or solution-state processing. This is based on work originated by Odell *et al.* [1] and developed by Bashir *et al.* [2–4] at Bristol University. A processing window (130–160 °C) in the melt phase was found whereby high-modulus products could be made by extensional flow and crystallization.

The techniques of production and the morphology produced by extensional flow are shown in Figs 1–4. In the original method of Odell, PE melt was extruded through a capillary at a critical temperature, which resulted in extended-chain fibrils being formed [1]. Blocking of the die with a needle valve led to complete solidification and this left an oriented plug in the capillary which could be pulled out after cooling (see Figs 1 and 5a). The plug had an interlocking shish-kebab morphology (see Figs 2 and 4), quite unlike that obtained from solid-state drawn PE. Odell *et al.* explained how such a predominantly chain-folded lamellar morphology, like that in Figs 2 and 4, could nevertheless yield a high-modulus product. Until then, it was believed that a high proportion of extended-chain material was necessary to produce high modulus from a flexible-chain polymer [1] and that it was not possible to produce high-modulus materials directly from melt processing of flexible-chain polymers [9]. Thus, the blocked plug work [1] demonstrated a principle, namely that it was possible to obtain a high-modulus product from melt processing and that a high proportion of extended-chain material was not necessary.

However, the die-blocking process was not a continuous one. Bashir, Odell and Keller [2–4] transformed this into a continuous melt-based process for producing high-performance PE. Two approaches were developed. In the first method, the melt was extruded in the temperature regime in which the fibrils were known to be formed and instead of blocking the die with a needle valve, it was found that an oriented filament with the shish-kebab morphology could be continuously wound up under certain conditions.

The PE used in Odell *et al.*'s original blocked-plug work was not suitable for the continuous production of an oriented filament. For the continuous formation of oriented filaments, it was necessary to use a PE which contained a high molecular weight tail in its molecular weight distribution [2, 3]. Otherwise, the filament broke frequently. It must be made clear that, although the process shown in Fig. 3 has a resemblance to ordinary melt spinning, the conditions required are very different [2, 3]. The as-spun fibres from normal melt spinning of flexible-chain polymers, (in contrast to liquid-crystal polymers), are not oriented and have to be post-drawn in the solid state to induce orientation [9]. This is because flexible-chain polymers such as PE have short relaxation times compared with liquid-crystal polymers and therefore disorient rapidly.

In the second variation of this continuous melt

Dedicated to professor Andrew Keller, FRS, after retirement, as a mark of appreciation for his contributions to the understanding of polymer crystallization, and for allowing us to learn about the subject and encouraging our investigations in a general research environment at Bristol.

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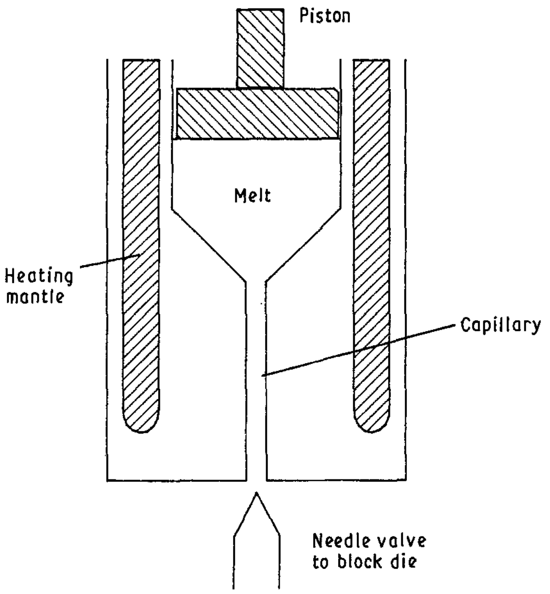

Figure 1 Schematic diagram showing the production of high-modulus oriented plugs. The following sequence is used: (i) melt extrusion conditions are set up (150 °C), (ii) extrusion temperature is lowered, (iii) at a certain temperature, extended-chain fibrils are formed in the melt and this can be detected as the extrusion pressure rises, (iv) at this juncture, the die is blocked with the needle valve and the piston speed is turned up; this causes the pressure to rise rapidly and it leads to complete blockage and crystallization of the remaining melt in the capillary and the barrel, (v) the needle valve is removed and the solidified billet which is attached to the oriented plug in the capillary is pushed out by the piston. The transparent, rigid plug left in the capillary (0.8 mm diameter, 5 cm long) can be extracted by pulling on the solidified billet pushed out of the rheometer.

process, it was found that pre-formed, unoriented PE fibres or films with the correct molecular weight distribution could be drawn above the conventional melting point in the temperature regime 130–160 °C, to give high-modulus high-strength filaments and tapes. This was called "melt drawing". Again, the melt-drawn PE had an interlocking shish-kebab morphology which was distinct from the morphology of PE drawn below 130 °C in the solid state.

Earlier, this morphology (Figs 2 and 4) was referred to as an "interlocking shish-kebab morphology" or a "zip morphology" [1–4]. In passing, it was even referred to as a "molecular composite" [3], although this is somewhat inaccurate. In this paper, we shall call it a "microfibrillar composite" for reasons that will be explained, and compare it with fibre and molecular composites. In particular, this morphology is a special kind of microfibrillar composite in that the reinforcing fibrils and the matrix are made of the same material, polyethylene. We shall show that such a composite has some special advantages, which are best appreciated by contrasting it with the other types of composites. Thus, part of this paper concentrates on the specific problem of making high modulus PE, while it also seeks to illustrate some general and interesting features in composites design.

First, fibre and molecular composites will be reviewed before considering the special polyethylene microfibrillar composite just mentioned.

2. Types of polymer composites

2.1. Fibre composites

These consist of high-modulus fibres (e.g. glass, carbon, polyethylene and Kevlar^{R}) embedded in a matrix, which may be a thermoplastic or thermosetting polymer. The fibres may be discontinuous or continuous. For continuous-fibre composites, unidirectional pre-

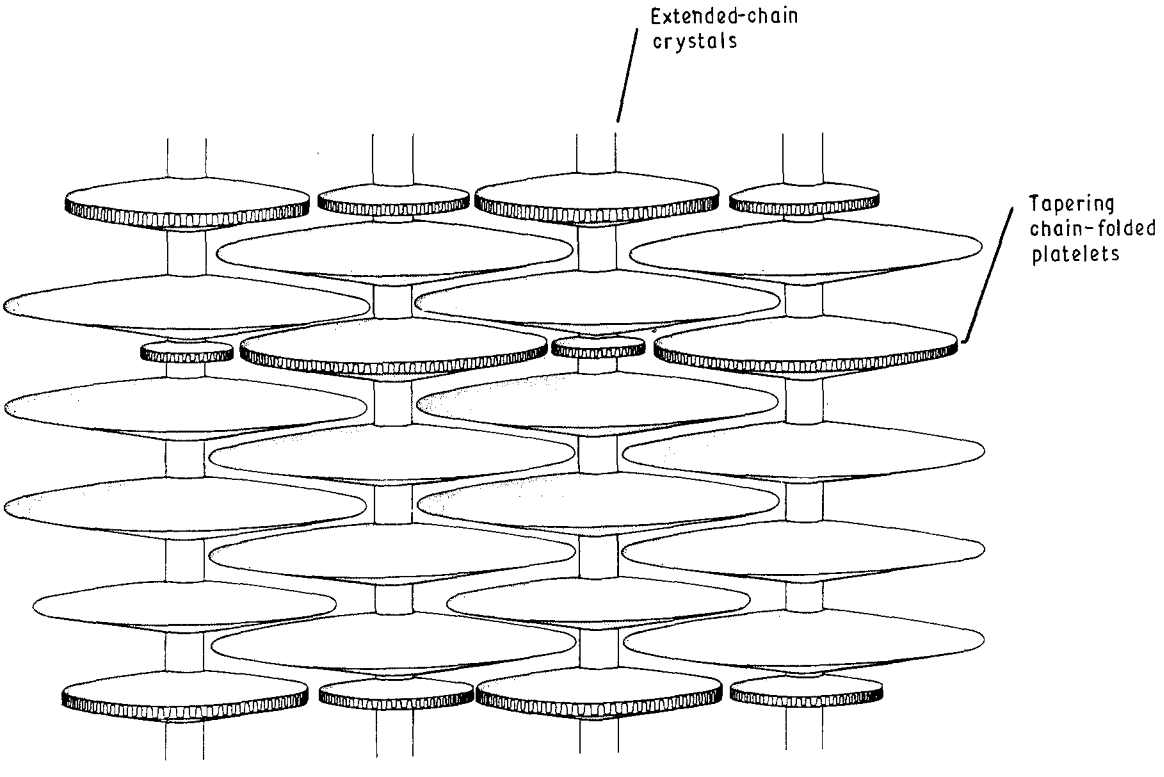

Figure 2 Schematic diagram of the interlocking shish-kebab morphology. See also Fig. 4 for a micrograph of the morphology. The assembly may be regarded as a microfibrillar composite of a special kind where the reinforcement (the extended-chain fibrils) and the matrix (the platelets) are of the same material.

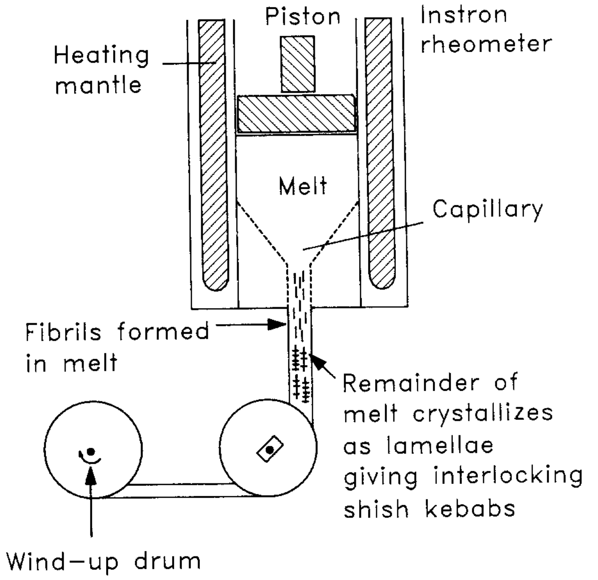

Figure 3 Continuous extrusion of an oriented filament with microfibrillar composite morphology. The conditions employed are dissimilar to conventional melt spinning. A PE with a high molecular weight tail in the distribution is required. The melt is extruded at a temperature at which fibrils are formed in the elongational flow field at the die entrance. If the filament is wound up under tension, the fibrils do not contract and melt after exiting from the die, and the remainder of the melt crystallizes on to the fibrils as lamellar overgrowths.

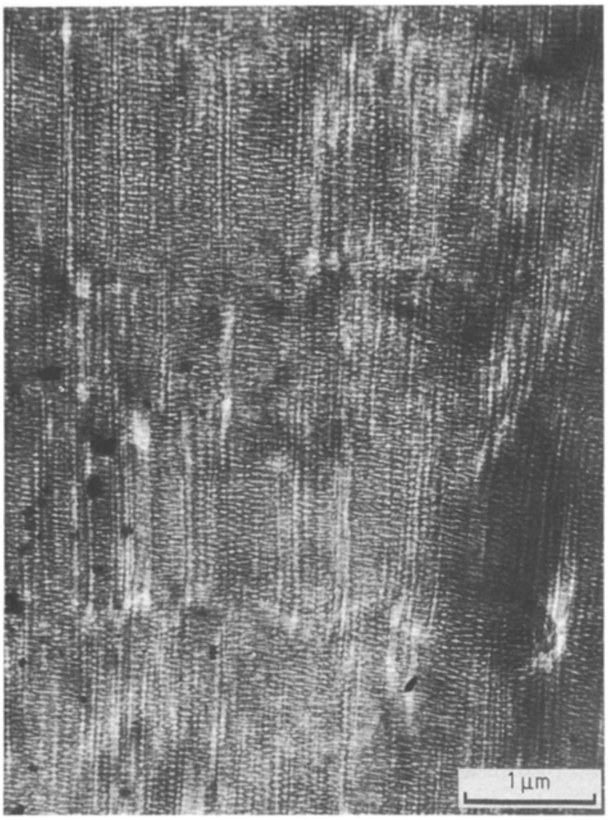

Figure 4 Transmission electron micrograph showing the microfibrillar composite morphology (courtesy of Dr M.J. Hill) in a section cut from the extruded filament. The fibrils have high aspect ratio but are present in low volume fractions. The bulk of the material is present as lamellar overgrowths and the chain direction is the same as the fibrils. The lamellae interdigitate and the resulting microfibrillar composite morphology is conducive to high modulus and strength. It is difficult to propagate cracks in both the transverse and longitudinal directions. The filament axis is vertical.

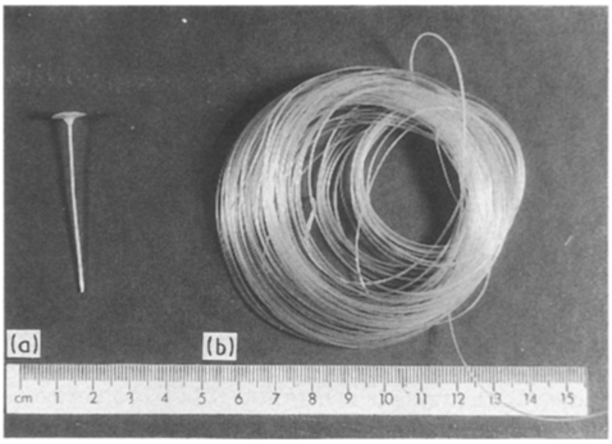

Figure 5 (a) The oriented plug formed by blocking the capillary has the same dimensions as the capillary (0.8 mm diameter, 5 cm long). (b) The thick, transparent, continuously extruded oriented filaments. Both samples have the microfibrillar composite morphology of Figs 2 and 4.

pregs or woven fabrics may be used. With uni-directional composites, 91% fibre-volume fractions are possible theoretically (with hexagonal packing of the fibres), but in practice fractions of only 50%–60% are attainable [10].

In fibre composites, the fibres are several micrometres in diameter (6 µm for carbon fibres, about ~ 30 µm for PE gel-drawn fibres). The matrix is usually a different material from the fibre, so that an interface is unavoidable. There are a few fibre composites where the fibre and the matrix are of the same material. For example, carbon–carbon composites are made for high-temperature applications, using carbon fibres and a resin such as pitch which can be carbonized [11, 12]. PE–PE fibre composites have also been reported using the gel-drawn PE fibres and a lower molecular weight PE as matrix [13].

In fibre composites, the high-modulus fibres carry most of the load. The fibre–matrix interface controls many properties [14]. Poor adhesion leads to poor stress transfer and fibre pull-out [14]. This is particularly the case with the gel-drawn high-modulus PE, where the poor adhesion to epoxy matrices [15], leads to low interlaminar shear-strengths (ILSS). In cases where the fibre and matrix are brittle materials (e.g. carbon–epoxy), too strong an adhesion is not desirable as it can lead to cracks propagating straight through the fibre and matrix [14]. Thus, to obtain a composite with high modulus and good toughness, an intermediate degree of adhesion is preferred, in cases where the fibre and matrix are both made of brittle materials, as fibre debonding can be a toughening mechanism [14].

The predominant mode of failure [15] of fibre composites is intralaminar shear (splintering of plies) or interlaminar shear (shearing between plies in a laminate). For carbon–epoxy composite, typical ILSS values range between 70 and 100 MPa [16]. For PE–epoxy composites [17], the ILSS is typically about 30 MPa.

2.2. Molecular composites

These consist of a molecular dispersion of a rigid, rod-like molecule inside a matrix of low-modulus polymer [18]. The idea is similar to a discontinuous or chopped-fibre composite, except that the reinforcement is at the molecular level. As with chopped-fibre composites, a high aspect ratio (length to diameter ratio) is necessary for effective reinforcement, which means that the molecules should be of sufficient molecular weight and they should not aggregate by phase separation.

Krause *et al.* [19] demonstrated a PBZT–ABPBI molecular composite, where the PBZT (polybenzbisthiazole) was the rigid-rod molecule which was used to reinforce ABPBI (poly(2, 5 (6) benzimidazole) which was the relatively flexible coil polymer. The PBZT and ABPBI were dissolved in a common solvent, followed by spinning and coagulation, giving a composite with a modulus of 120 GPa under certain conditions. The modulus of PBZT fibres is 300 GPa, while the modulus of unreinforced ABPBI is 35 GPa [19]. Even in the favourable case where a composite modulus of 120 GPa was obtained, the dispersion of rigid rods was not truly molecular, but the aggregation of the PBZT was minimized to the extent (less than 3 nm) that a sufficiently large aspect ratio for the reinforcement was obtained. There was a critical total polymer concentration of about 2%–6% (with respect to the common solvent), above which the PBZT formed a liquid-crystal phase. Phase separation led to globules of PBZT dispersed in the matrix polymer. The effective aspect ratio was thus reduced, so the PBZT ceased to be a reinforcement under the conditions where this happened, and the modulus of the composite was lowered to 11 GPa [19].

Similarly, Takayanagi has solution-blended the rigid-rod polymers poly(*p*-phenylene terephthalamide) and poly(*p*-benzamide) with nylon 6 and nylon 6, 6 to form molecular composites [20]. Although these are interesting examples, the system is of little practical use, as it involves using less than 2%–6% polymer concentration, and strong acid solvents. Apart from the impracticalities of solution blending, there are inherent problems in taking a rigid-rod polymer in sufficient concentration (with respect to the matrix polymer) and dispersing it at a molecular level [21]. Rigid-rod molecules have a tendency to form a liquid-crystal phase at concentrations of a few per cent, and this automatically reduces the aspect ratio and hence the reinforcement efficiency.

Ballauf has explained why rod-like and coil-like molecules are virtually incompatible [21]. For an isotropic composition of rod-like and coil-like molecules, the Flory–Huggins theory may be applied which leads to the conclusion that compatible mixtures in the isotropic state are exceptions to the rule, the exception being when strong intermolecular (for example, dipolar or hydrogen bonding) interactions are present between the two components [22]; for compositions where a liquid-crystal phase can be formed, "entropic demixing" causes additional incompatibility [21].

Thus, phase separation makes the attainment of true molecular composites by solution blending difficult. At best, the solution-blending method leads to aggregates of the reinforcing polymer with dimensions of the order of 10 nm; in fact, certain authors prefer to use the term nanocomposites rather than molecular composites in such instances [23].

Attempts have also been made to overcome the problems inherent in the solution dispersion method of forming molecular composites by *in situ* polymerization of rigid-rod polymers within a polymer matrix [24]. Conceptually, the process involves blending two compatible coil-like polymers and thermally isomerizing one of the polymers to a rigid-rod, thus providing the reinforcing element of the composite. Wallace *et al* [24] report the possibility of using a coil-like aromatic polyisoimide which is compatible and soluble with an amorphous matrix-polymer or thermosetting oligomer, and then transforming the polyisomide to the corresponding rigid-rod polyimide in the solid composite state. No mechanical properties were reported [24]. Even in this approach, a solvent was still needed initially to disperse the rigid-rod precursor polymer within the matrix polymer.

Finally, another approach that has been tried is to make melt-processible molecular composites so that the difficulties of solution blending are avoided. The method involves synthesizing segmented or block copolymers composed of rigid-rod segments which act as the reinforcing phase and flexible-coil segments which behave as the matrix [25–27].

2.3. Microfibrillar composites

Here, the reinforcement is present in the form of micrometre or sub-micrometre diameter fibrils, that is, an intermediate scale between fibre and molecular composites. These can be generated *in situ*, by extensional flow and crystallization. Two types of such composites will be considered, one in which the reinforcement and matrix are different materials, and another in which the reinforcement and matrix are different materials, and another in which the reinforcement and matrix are the same material.

2.3.1. Micro-fibrils and matrix of different materials

The most common way to produce such composites is to extrude a blend of a thermotropic liquid-crystal polymer (LCP) and an ordinary polymer such as polystyrene, nylon or polyester [28–30]. When a blend of the right composition is extruded or injection moulded, the liquid-crystal polymer becomes oriented and can form needle-like fibrils which are embedded in a matrix of isotropic polymer.

Blizard and Baird showed that extrusion of a 30% LCP–70% polycarbonate blend led to fibril formation [31]. The fibrils were 1–10 μm in diameter. The fibril formation by the LCP in the blend depended on having a critical volume fraction and application of an extensional flow field. No fibrils were formed when the blend was subjected to a shear flow field [31].

Kiss [32] has blended 30% by weight of LCPs with polyether sulphone (PES). Extruded strands of neat PES had a modulus of 2.6 GPa and a tensile strength of 69 MPa. However, an extruded strand of a 30% LCP–PES blend had a modulus of 11.8 GPa and a strength of 140 MPa. The LCP formed domains which could be needle-like fibrils (with 2–5 μm diameter and high aspect ratio), or sheet-like structures [32]. Interfacial adhesion between the PES matrix and the LCP fibrils was reported to be poor, leading to fibril pull-out, but considerable enhancement of the mechanical properties of the matrix polymer occurred nevertheless [32]. Some of the *in situ* microfibrillar composites made by Kiss gave strengths of over 130 MPa and moduli over 6 GPa, which is well into the range of chopped glass-fibre engineering resins [32]. Further advantages with these *in situ* reinforcements over chopped fibre-reinforced thermoplastics was that the melt viscosity was lowered by the addition of LCP. Fibre breakage which occurs with chopped-fibre reinforced thermoplastics during extrusion, thereby reducing the fibre aspect ratio, was not a problem. Machine wear (encountered with resins containing abrasive glass or carbon fibres) can also be avoided [28].

In-situ polymerization has also been used to make microfibrillar composites. Here, the idea is to form needle-like crystals of a monomeric species in a polymer matrix during processing and then to polymerize the monomer to a highly oriented, fibrous polymer. Monomers with conjugated triple bonds such as di- and tri-acetylenes can be polymerized in the solid-state to yield fibrillar extended-chain polymeric single crystals with a negative thermal expansion coefficient and very high modulus and strength. A microfibrillar composite made by *in situ* polymerization has been reported by Baughman *et al.* [33]. Polyacetylene and polydiacetylene fibrils were formed by *in situ* solid-state polymerization of monomer crystals in a polyvinylidene fluoride matrix in order to produce composites with near-zero thermal expansion coefficient. The mechanical properties of the composite were not reported [33].

In passing, it is also noted that one method of making metal fibre–metal matrix composites is based on *in situ* unidirectional solidification and crystallization. A metal bar of eutectic (or off-eutectic) alloy is melted and cooled, which causes one component to precipitate out as rod-shaped or plate-shaped material [34, 35]. For example, rods of chromium can be grown in a nickel matrix from a 40:60 Ni–Cr alloy [34]. Sprenger *et al.* [36] reported the *in situ* growth of continuous molybdenum fibres with approximately 2 μm × 5 μm rectangular cross-section in a Ni_3Al matrix. Note that melting is required, but significant extensional flow is not necessary to produce this type of metal microfibrillar composite; in contrast, with polymers, extensional flow is usually required for *in situ* fibril formation.

2.3.2. Micro-fibrils and matrix of the same material

This is a relatively little-known concept and it is the purpose of this article to highlight and contrast some of the properties of such a composite. We shall use Odell's blocked plugs, the melt-extruded filaments, and the melt-drawn tapes and fibres with the shish-kebab morphology as examples of microfibrillar composites of the type where reinforcement and matrix are of the same material.

To recapitulate, Odell's discontinuous plugs attained moduli of 50–90 GPa [1]. The continuously extruded filament [2, 3] attained moduli of 10–20 GPa, and surprisingly high strengths of 1.2 GPa (this has to be contrasted with unoriented fibres made by normal melt spinning, which have moduli of about 0.1 GPa and strengths of 0.01 GPa). The melt-drawn tapes attained higher moduli of 60–80 GPa and strengths of 1.5 GPa [4].

We shall just refer to the continuously extruded thick filament in Fig.5 for the remainder of the discussion, although what is said applies to the blocked plugs as well as the melt-drawn PE, as they have common morphological features.

The strength of commercial gel-drawn fibres is typically greater than 3 GPa but this is for ~ 30 μm diameter fibres. To attain 1.2 GPa strength in a thick filament is thus remarkable. Further, the filament did not splinter, which was unusual because normally a uniaxially oriented polymer would splinter if the specimen is thick. The reason is that with the morphology of Fig. 4, crack propagation in the transverse direction is arrested by the fibrils, while in the longitudinal direction, it is difficult for a crack to thread its way through the intermeshing lamellae. In principle, if such a morphology was established in a wide sheet-form, it can be expected that such a sheet would have not only high modulus and strength in the direction of the fibrils but it would have good transverse properties, resistance towards splintering, as well as toughness.

Thus, the microfibrillar composite of Fig. 4 is of a special kind: firstly, the fibrils and the matrix are of the same material, polyethylene; secondly, the matrix is also oriented in the same direction as the fibrils; thirdly, the fibrils in the composite are generated by *in situ* flow and crystallization. The consequences of these three features are discussed.

Unlike composites where the fibre and matrix are of different materials, the adhesion problem is not present here, as the matrix, being the same material, can be molecularly continuous and co-crystallizes with the fibril. However, despite this molecular continuity, the material is not a macroscopic single crystal of PE but is like a composite, as there is still an interface between the lamellae that have grown from adjacent fibrils (Fig. 4). It is noted that while a continuous, macroscopic single-crystal of polyethylene could attain the ultimate modulus of polyethylene (240 GPa by X-ray and 358 GPa by Raman methods, [37, 38]), in practice such a material may not be so useful because it would be prone to splintering due to the low shear strength and the poor transverse tensile strengths.

The next feature is that the matrix in this composite is also oriented and shares the load. Odell has described the conditions needed to extract the optimum performance from such an assembly [1]. The principal requirements are that the fibrils should be fine and be spaced no more than 100 nm apart, so that the lamellae do not twist and the chain axes in the lamellae always remain parallel with the fibrils. It is better to have a large number of fine fibrils spaced the optimum distance apart for interdigitating, than have aggregation of the extended-chain material into very thick fibrils [4]. The interdigitating itself is caused by the increasing supercooling (caused by a pressure increase in the blocked-plug experiment or thermal cooling of the extruded filament in the continuous experiment) which leads to lamellar tapering. It is well known that the lamellar thickness decreases with supercooling [39]. The resulting wedge-shaped lamellae thus interpenetrate to give the morphology of Fig. 2.

The fibril diameter in Fig. 4 is of the order of 5–25 nm and the aspect ratio is at least about 200–600. The aspect ratio may be greater than this as it is not clear from the micrograph in Fig. 4 where the fibrils end; it is possible that the fibrils merely dip below the surface of the specimen and so are not clearly imaged. In melt-drawn films, thicker fibrils with diameters up to 150 nm were formed due to aggregation [4]. The intermolecular separation of PE chains in an orthorhombic crystal lattice is about 0.5 nm; hence, these 5–25 nm diameter fibrils in the PE–PE microfibrillar composites are closer to the dimensions in molecular composites as the fibril diameter here is substantially smaller than the 1–10 μm (1000–10 000 nm) diameter fibrils formed in the microfibrillar composites from the liquid-crystal polymer blends mentioned previously in Section 2.3.1.

It is interesting to compare this PE–PE composite with a uni-directional fibre composite consisting of, say, carbon fibres and epoxy resin. In the latter case, analysis shows that the composite modulus parallel to the fibre direction can be described by the Voigt model which assumes parallel coupling of stresses and equal strains in the matrix and the fibre [14]. For short fibres, the composite modulus is given by

$$E_c = E_f V_f + E_m V_m - \frac{V_f E_f^2 \varepsilon}{4\tau s} \qquad (1)$$

where E_f and E_m are the tensile moduli of the fibres and matrix, V_f and V_m are the volume fractions of fibre and matrix, s is the aspect ratio of the fibres, τ is the interfacial shear stress and ε is the strain in the fibre which is equal to the strain in the matrix, according to the Voigt model [34].

For continuous fibre composites, $s \to \infty$, and so the third term on the right of the equation can be neglected; the composite modulus is then given by a simple Rule of Mixtures (ROM), $E_c = E_f V_f + E_m V_m$, which for high-volume fractions of high-modulus fibres further reduces to $E_c = E_f V_f$, as there is such a disparity between the moduli of the two components. The matrix carries a negligible portion of the load and the composite tensile-modulus parallel to the fibre direction is entirely fibre dominated.

However, the modulus of the extruded filament or the oriented plug produced by Odell cannot be accounted for by the extended-chain fibrils alone, because this is only present at a volume fraction of about 5%. Hence, the composite modulus cannot be obtained from the ROM. For example, Odell's oriented plugs had moduli of 50–90 GPa. Taking 240 GPa [37] as the approximate modulus of the fibrils and even after assuming continuous fibrils, an ROM modulus would give only $0.05 \times 240 = 12$GPa. Clearly, the matrix is also contributing to the modulus of the microfibrillar composite assembly.

A characteristic of the uni-directional fibre pre-preg is that it splinters easily. The critical angle for failure for off-axis loading [40] is given by $\theta_{crit} = 1/2 \arcsin (2\tau/\sigma_c)$, where τ is the matrix or interfacial shear strength and σ_c is composite tensile-strength (assuming-axially-aligned fibres). For high-strength fibres and high-volume fractions, the critical angle would be very low, typically 2°–5°. If the loading axis deviates from the fibre axis by more than the critical angle, the uni-directional fibre composite fails prematurely by interfacial or matrix shear rather than by tensile fracture of the fibres. Hence, uni-directional fibre pre-pregs cannot be used for structural applications and multi-directional laminates have to be made by cross-plying.

If instead of an isotropic matrix, a high-modulus, anisotropic matrix which was aligned with the fibre axis was used, the transverse properties would be even worse than having a uni-directional fibre composite with an isotropic matrix. Such a composite can be made by using, for instance, carbon fibres and a thermotropic liquid-crystal polymer as the matrix. Surface forces spontaneously align the liquid-crystal polymer molecules in the direction of the carbon fibres [41].

In contrast, the microfibrillar PE–PE composite can withstand off-axis loading better, despite the matrix being oriented in the fibril direction, because of the intermeshing lamellar assembly. It is thus clear that the microfibrillar composite morphology of Fig. 4 is unusual in having the matrix oriented in the same direction as the fibrils without having a detrimental effect on the transverse properties.

A particular problem with oriented polyethylene is that it creeps under constant loading. The gel-drawn PE fibres can give the highest moduli and strength, but have the worst creep properties. This is to be expected as the gel-drawn fibre is mostly extended-chain polyethylene. The solid-state drawn spherulitic polyethylene has better creep properties than the gel-drawn type. Detailed work on creep properties of the microfibrillar PE was not conducted but it would appear that this morphology may offer even better creep resistance. This is an area that requires more investigation.

In common with fibre composites, these PE filaments show acoustic emission when put under high stress. The 0.8 mm diameter extruded filament (Fig. 5b) could not be broken by hand. (On the other hand, an unoriented PE filament of similar diameter but with a spherulitic morphology extruded under different conditions is very easy to break by hand). However, in trying to break the oriented filament by hand, crackling noises were emitted by the filament. This was due to some of the fibrils breaking, without the whole filament breaking. It is similar to the behaviour of a continuous-fibre composite where, in fact, acoustic emission can be used to monitor fibre breakage during tensile testing [34]. In a fibre composite, as the load increases, some of the fibres can be heard breaking at strains below the failure strain of the entire composite [34]. Thus, it is entirely apt to regard these melt-extruded filaments as a composite with microfibrils.

Solid-state drawn PE splinters if ultra drawn, unless the fibres are fine. However, it was reported at the time that these melt-extruded filaments and oriented plugs do not fibrillate [1–4]. Since that work was reported, subsequent findings show that this statement needs some qualification. It is still true that these filaments do not fibrillate in the sense that they do not splinter catastrophically. However, vigorous abrasion of the extruded filament can lead to the peeling of fine fibres from the surface (Fig. 6), but the apparent tensile strength does not seem to be affected by these surface blemishes. The surface fibres only form during vigorous abrasion, but do not continue to propagate, even if the filament is loaded in tension afterwards. Again, this must arise due to the complex intermeshing morphology of Fig. 4 which does not allow fine fibres to be detached easily from the surface.

Normally, the filaments are very transparent (Fig. 5), but winding round pulleys with small radii of curvature after extrusion, leads to compressive failure and these show up as microscopic kink bands (Fig. 7). High-modulus polymers are particularly poor in compression. Kevlar fibres and even carbon fibres are not as good in compression as they are in tension, and oriented PE fibres are even worse in this respect [42]. The thick filament shown in Fig. 5 was wound round a pulley with a diameter of 5 cm and despite the compressive damage, it still showed a remarkably high tensile strength, as already mentioned. It would be interesting to extrude a hollow filament with this morphology, as this would lead to filaments which would be good in tension and compression. Melt processing allows the possibility of extruding stiff, hollow fibres of PE; indeed, it is conceivable that it would be possible to extrude a light, stiff tube of PE, which, like bamboo, would be good in tension and compression.

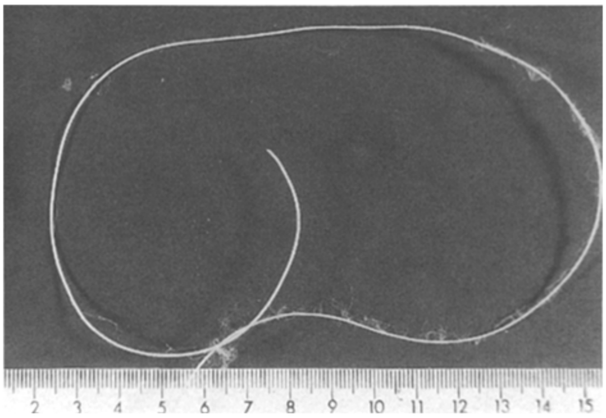

Figure 6 The extruded filaments of Fig. 5 do not splinter. However, vigorous abrasion leads to fine fibrils being peeled from the filament surface. The filament diameter is 0.8 mm.

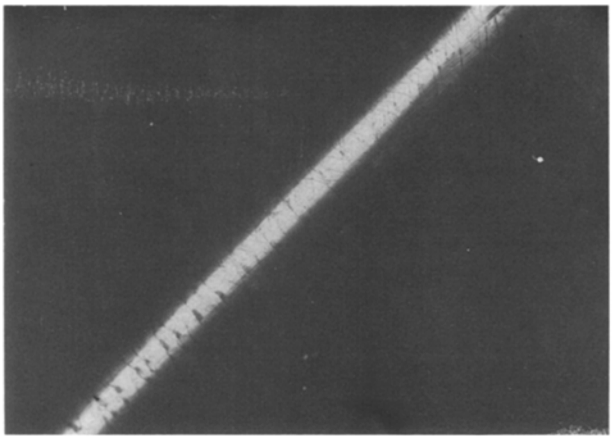

Figure 7 The extruded filaments show compression damage due to winding round pulleys. This manifests itself as microscopic kink bands (optical micrograph taken between crossed polars). The filament diameter is 0.8 mm. Fibre axis is 45° to polarizer axes.

The other unique feature of these microfibrillar composites is their method of formation. In a continuous fibre composite, the fibres have to be impregnated with the matrix and in the case of thermoplastic matrices, impregnation itself is a problem, as polymer melt viscosities are generally high. In the case of molecular composites, solution blending and *in situ* polymerization have been tried. In the case of the microfibrillar PE–PE composite, one may avoid the mixing problem by using a polyethylene with a small amount of inherent high molecular weight tail in the molecular weight distribution [3, 4].The fibrils are created from the high molecular weight tail during processing, by flow-induced chain extension and crystallization [3, 4].

Previously, we explained how the extensional flow in the entrance to the capillary (Fig. 1) led to chain extension, particularly of the high molecular weight component, which then crystallized and formed the fibrils [2–4]. A similar mechanism was believed to operate during melt drawing [4] between 130 and 160 °C which was an alternative method of producing the morphology of Fig. 2. This explanation is still valid, but in the light of further developments, it is felt that there are more subtleties involved. In both cases (extrusion and melt drawing) it was observed that extended-chain crystals were only formed in the temperature region 130–160 °C. It has been known for some time that PE shows a hexagonal phase at high temperatures and high pressures [39]. Normally, PE undergoes an orthorhombic crystal to isotropic melt transition on heating. However, under high pressure, it undergoes an orthorhombic crystal → hexagonal mesophase → isotropic melt transition [39]. Further, it has also been shown that the hexagonal phase can be stabilized by maintaining a tension on the PE fibrils up to 180 °C [43].

Thus, melt extrusion or melt drawing in the zone 130–160 °C probably leads to the formation of a hexagonal mesophase of extended chains which is stabilized by the applied tension during filament wind-up or during melt drawing, and this then transforms to the normal orthorhombic phase after cooling below

145 °C. This was mentioned in the original work without direct evidence [4] but further work at Bristol on the hexagonal mesophase [43, 44] supports this explanation.

Although we have used PE to illustrate the formation and properties of microfibrillar composites where the fibre and matrix are of the same material, it is worth mentioning that there are other examples where different regions of the same polymer chain form the fibres and the matrix, so as to mimic the behaviour of a two-phase composite. In an extruded plug of the triblock (styrene–butadiene–styrene) copolymer, it has been shown that regular hexagonal lattices are formed with the polystyrene segments forming 15 nm diameter rods which are embedded in a polybutadiene matrix [45]. Examples of natural composites where the low-modulus matrix and the high-modulus fibres are parts of the same molecules are the β-keratin of feathers and the α-keratin of hairs [46, 47]. Again, in these examples, the problem of bonding between the two phases does not arise. The PE–PE microfibrillar composite shares some features with these examples, yet there are other aspects which make it different. The PE molecule does not have any functional groups or segments which therefore could phase-separate for this reason. Phase separation to form the constituent fibrils and the matrix of the composite occurs here due to the molecular weight distribution, with the high molecular weight tail contributing to the fibril component.

3. Conclusion

The purpose of this paper was to update and highlight the significance of a novel morphology obtained with melt-processed PE. Previously this was referred to as an interlocking shish-kebab morphology for obvious reasons, but here it has been renamed a PE–PE microfibrillar composite.

These PE–PE microfibrillar composites have at least three distinguishing features.

(i) The fibrils and the matrix are of the same material, yet the fibrils are distinct and separated from each other. Fibre–matrix adhesion is not a problem, due to epitaxial crystallization and the molecular continuity of the phases.

(ii) The matrix is also oriented in the same direction as the fibrils, but at the same time, this does not lead to poor transverse properties.

(iii) The fibrils are created *in situ*, by extensional flow and crystallization, and have high aspect ratio. In principle, this means there is no need for mixing different components, as the ingredients can be present in the one polymer and it just has to be processed under suitable conditions. The high molecular component contributes predominantly to fibril formation.

This approach to polymer composites is worth developing, although clearly it cannot be used for all materials. Much work needs to be done in synthesizing PE with the optimum molecular weight distribution. Further, the work needs to be extended to extrusion of sheet, tube and other profiles.

There are several approaches to producing high-performance polyethylene. These are solid-state drawing of melt-crystallized PE fibres, ultra drawing of gel(solution)-crystallized PE, melt extrusion and melt drawing. Each approach has its merits and limitations. The gel-drawn PE fibres have given the highest moduli and strength. However, the axial modulus and strength are not everything, and it would seem that if balanced properties are sought, the microfibrillar composite offers good scope. This complex morphology allows the possibility of obtaining high modulus and strength, without compromising transverse properties, toughness and creep resistance.

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