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Review

High-strength polyethylene fibres from solution and gel spinning

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There are many recent reports in the literature of high-strength, high-stiffness polyethylene fibres produced by a variety of techniques, all of which involve at some stage crystallizing the polymer (invariably a high molecular weight material) from solution. In this review we try to place these reports in their proper context and to show how and why the various techniques have been developed. To do this we present brief historical reviews of two distinct subjects: the drawing of single-crystal mats and the preparation of "shish kebabs". Both of these have, when used in conjunction with very high molecular weight material, led to very strong and stiff fibres. We then describe the recent gel spinning techniques and arrive at the conclusion that there are essentially just two distinct processes involved: the solid state deformation of single crystals, and the crystallization of pre-extended chains to form shish kebabs. Either or both of these processes can occur in gel spinning. In addition to the scientific subject some technical aspects, including material from the patent literature, are also covered.

1. Introduction

All linear polymers are, by virtue of their covalent bonding, potentially very strong and stiff. However, until recently this potential has not been realized in flexible chain systems such as polyethylene. In the course of the conventionally-applied drawing processes the chains do not become sufficiently extended, as opposed to becoming merely oriented as diagnosed through conventional tests (e.g. X-ray diffraction and birefringence). Fig. 1 serves as an illustration of the distinction between high orientation (Fig. 1a) and full chain-extension (Fig. 1b), the prerequisite for maximum strength and stiffness. Over the past few years, however, there have been several reports of the achievement of increasingly strong and stiff polyethylene fibres [1]. These probably began in the mid-1970s with the work on drawing of melt-crystallized material to very high draw ratios (~ 30) by the group at Leeds under Ward [2–4]. This work was concerned with polyethylenes of normal molecular weights 10^4 to 10^5; moduli of up to ~ 70 GPa were reported. This was followed by a number of further developments involving various methods of fibre drawing and solid-state extrusion, and the gradual introduction of the totally different route involving solution (including gel-state) processing attaining moduli up to 200 GPa. In these latter developments special high molecular weight materials (10^6 and more) played an increasingly important part.

It is convenient at this point to introduce a "scale" of stiffness and strength for polyethylene, since we shall inevitably refer often in this review to high moduli and strengths; we have in Fig. 2 drawn a scale on which we have marked some of the more important landmarks in stiffness and strength of polyethylene fibres, both theoretical and those actually achieved. We also list in Table I the properties of materials more commonly thought to possess high stiffness and strength. It should be apparent that the work on solid-state deformation of melt-crystallized polyethylene has produced materials as stiff as aluminium or glass but with somewhat lower strength. Work on solid-state

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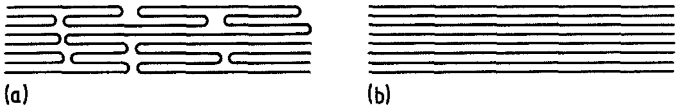


Figure 1 A sketch showing how high molecular orientation can be achieved (a) without and (b) with high molecular extension.

deformation has continued in many centres around the world, and higher draw ratios (or in the case of solid-state extrusion, extrusion ratios) have been achieved leading to improved strengths and stiffness [5–8]. The stiffness of fibres prepared by drawing melt-crystallized polyethylene has been shown to depend primarily on the draw ratio, higher draw ratios giving stiffer fibres. On the other hand the strength appears to depend much more on the polymer molecular weight; at a given draw ratio higher molecular weights give higher strengths. In particular, the strength which can be obtained by these methods is quite low, since only comparatively low molecular weight polymers can be successfully processed to high deformation ratios. Since in terms of what can be achieved in modulus and strength (although not necessarily in terms of ease and cost of manufacture) these methods have largely been surpassed by the newer solution-processing techniques, we shall say no more of them in this review which will be confined to solution processing and to fibres arising therefrom.

The solution methods allow processing of very high molecular weight polymers, and as a result immediately give access to much higher strengths for a given stiffness. Specifically we shall try in this article to guide those not directly involved in the subject through the work on high-modulus, high-strength fibres from solution (and gel) processing of ultra-high molecular weight polyethylene (UHMW–PE). It is the purpose of the present survey to clarify at least one aspect of the field, not only by describing its present status but also by providing a historical survey to show how each stage of the development and each idea raised in the past fits in its place, or has been overtaken by later events. The references to be quoted should provide a representative selection of individual works, but we claim no completeness. Summarizing articles [9–13] should be particularly useful for the appreciation of the state of the subject at the particular date from the particular viewpoint of the author concerned, and also for providing a more comprehensive list of references.

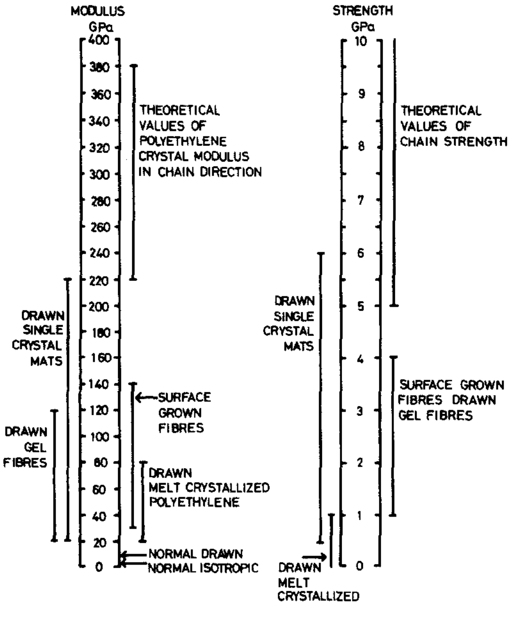


Figure 2 Scales of tensile modulus and strength of polyethylene.

Basically there are three routes by which UHMW–PE can be successfully processed to make strong stiff fibres from solution; all involve first dissolving the polymer. At one extreme the polymer is crystallized to form lamellar single crystals, and these are then formed into a film which is drawn. At the other the polymer is crystallized as a continuous array of fibrous crystals ("shish kebabs") in which the chains are predominantly highly extended and which themselves already possess good mechanical

TABLE I Properties of some strong, stiff materials

Material	Tensile modulus (GPa)	Breaking strength (GPa)
Steel	~ 210	1 to 4
Drawn silica fibres	80	6.0
Whisker crystals	200 to 500	10 to 20
"Kevlar" fibres	60 to 120	~ 2.5
Carbon fibres	400	~ 3
Drawn melt-crystallized polyethylene fibres	~ 70	~ 1
Drawn gel fibres of ultra-high molecular weight polyethylene	~ 120	~ 4
Drawn single-crystals mats of UHMW–PE	~ 200	~ 6

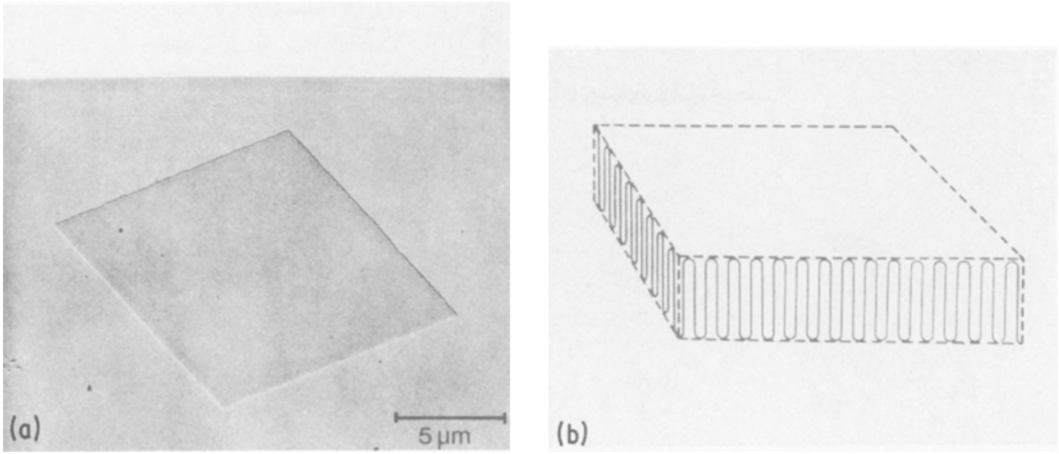


Figure 3 (a) An electron micrograph of a polyethylene single crystal; (b) a sketch indicating the arrangement of molecules within such a crystal.

properties. The third and technologically most useful group of methods involves making a gel from the polymer solution, and the subsequent processing of it to form a fibre.

In this review we shall first briefly introduce the principal structural concepts pertaining to polymer crystallization (already mentioned in the above listing), for the reader who may not be familiar with them. Following this we shall present an historical survey, which we consider essential as the emphasis and understanding have been changing over the years. We shall then look in greater detail at the various gel processing methods which have acquired particular prominence in the latest literature. Finally we shall make some comments about the morphology and properties of the fibres. In particular we hope to convey that in our opinion, despite many perplexing differences in detail, various methods of solution-based fibre production (and the nature and properties of the resulting fibres) rely essentially on similar basic principles. We thus hope to remove much of the confusion and mystique which currently seems to surround the subject.

2. Polymer crystal morphology and fibre formation

The basic mode by which flexible chains are crystallized is through the formation of lamellae within which the chains are in a folded conformation. This is most conspicuously apparent in crystallization from solution, where the whole phenomenon was first recognized. Here, in the case of the usual stationary solutions, the crystals precipitate on cooling to form a suspension of platelets which individually have the appearance shown in Fig. 3a, with the underlying folded molecular configuration as in Fig. 3b. (Similar lamellae result also on crystallization from the melt, but there they give rise to more complex aggregates, the spherulites, which will not concern us in this article.) In Fig. 3b the chain-folded structure is drawn in an idealized manner. The issue of how far the folds are regular and adjacently re-entrant is a subject of much debate, which will not, however, be of consequence for the present article

Another mode of crystallization is that induced by chain stretching, which in the case of solutions involves flow. This is most simply realized by stirring, the method by which the effect was originally discovered [14]. Here the solution is stirred at a temperature which is too high for the usual chain-folded crystals to form in a quiescent state; nevertheless crystallization can be promoted by stirring-induced flow, where the crystals precipitate on to the stirrer in the form of fibrous aggregates. The resulting crystals, generally believed to arise from prestretched molecules (some qualifications will be apparent later), have an overall fibrous character with the chain direction along the fibre axis. However, within the fibrous envelope there is a profusion of platelet-based structures where the platelets are attached to an intrinsically fibrous core (see Figs. 9 and 10 in Section 5). The molecular arrangement within the fibrous core is essentially of extended-chain type, while that within the platelets is folded. The interrelation between the core fibre and the platelets is complex and will be dealt with further below.

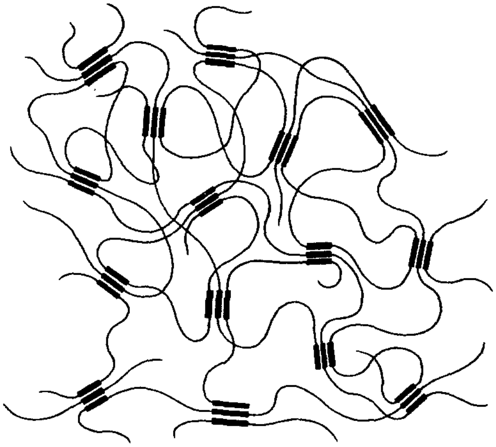


Figure 4 A sketch illustrating a gel with micellar junctions.

The whole fibre–platelet assembly is termed shish kebab. This type of crystallization occurs increasingly readily with higher molecular weights.

The third mode of crystallization is the one leading to gels. As will be described in the separate section devoted to it, there are various ways by which crystallization can give rise to gels. The common feature of them all is that the gels in question are swollen networks in which crystalline regions form the junctions. These junctions can themselves be of various crystal types; they can be chain-folded platelets, fibrous crystals (shish kebabs), still-unspecified precursors of such shish kebabs, or a special kind of crystal (possibly tiny micelles as in Fig. 4) of which we shall say more later. Whatever the nature of the gel junction, two factors promote gel-forming crystallization: increasing molecular weight of the polymer, and increasing concentration of the solution for a given molecular weight.

Clearly in lamellar single crystals and in gels the chains are not extended, and not even oriented with respect to any macroscopically defined direction. Hence the polymer in these two states has to be oriented and drawn, in order to align and extend the chains so as to form high-modulus fibres. A gel representing a macroscopically connected structure is clearly drawable in principle, as in fact it is being drawn in practical fibre production. This clearly does not apply to a suspension of single crystals. Nevertheless, the suspended crystal platelets can be sedimented into coherent layers where the lamellae usually lie all parallel. These so-called "single-crystal mats", even if made up of initially separate lamellar entities, may be drawable under appropriate circumstances owing to the unexpectedly high cohesion between the constituent layers. Both drawing of single-crystal mats and of gels will feature in what follows.

It is to be noted as a general guideline that for optimum final properties it is desirable to have draw ratios as high as possible, usually 20 to 100, and certainly in excess of the conventional "natural draw ratio" of 4 to 6 featuring in more traditional fibre drawing. Many of the developments centre round the attainment of such high values. This is greatly aided by the texture and morphology of the starting material. In the case of single-crystal mats the lamellae are predominantly parallel to the mat plane, and the draw direction, (as dictated by the macroscopic shape of the sample) is also in this plane. It follows from Fig. 3b that drawing takes place from an initial configuration where most of the chain is oriented essentially perpendicular to the draw direction; this is evidently favourable for the achievement of high draw ratios, which relies on the activation of plastic deformation of the crystals (discussed later). The gels are by their nature very loose networks which again lend themselves to high draw ratios and hence to high chain extension, which in general terms is the origin of the suitability of the gel consistency for fibre production.

Crystals which are fibrous *ab initio* (such as the shish kebabs) may not need drawing, but merely assembling in a macroscopic fibre form with as much extended-chain core component as it is possible to realize in the course of the primary crystallization. Indeed, historically much of the solution-based fibre production on a laboratory scale relied on this principle. It was then an unexpected twist of the story when it turned out that in much of shish kebab-based fibre formation, drawing is in fact involved through the intermediate agency of gel formation; this will become apparent in what is to follow. Moreover, a link has also evolved between drawing of single crystals and gel drawing in the practically most frequent cases where the gel junction crystals are of the chain-folded lamellar type. Thus, with the exception of single-crystal mats which arise from sedimentation of a genuine suspension (which will only be the case with dilute solutions impracticable for technological exploitation), all other solution-processing methods have the gel state as the common denominator, irrespective of the different structural variants within the gel state which might be involved. As gel formation is promoted by long chains, the emphasis on high molecular weight material follows naturally.

3. Historical survey

In this section we intend to give a very brief historical survey of the development of high-strength polyethylene from solution-processing routes, so that the significance of each stage along the tortuous path can be appreciated. Indeed it should be noted that as far as we are aware little if any of the early work [14–16] was carried out with the objective of producing strong, stiff fibres.

The drawing of single-crystal mats dates back to the work of Statton in the 1960s [15] who reported moduli of ~ 10 GPa and strength ~ 0.67 GPa; later workers in the 1970s [17–19] reported moduli of up to 50 GPa and strengths ~ 0.5 GPa. All this work was done using normal molecular weight polyethylenes. Meanwhile ultra-high molecular weight polyethylene (i.e. molecular weight $\sim 10^6$) was being used, notably by Pennings and his co-workers [14, 20–22] to produce shish kebab crystals from flowing solutions at temperatures above those at which single crystals could be grown; methods were developed to make continuous fibres, and by the late 1970s moduli of 5 to 10 GPa and strength 0.5 to 1 GPa had been produced using the "free-growth" method [21]. The major breakthrough came with the development of the "surface-growth" method of Zwijnenburg and Pennings [23, 24] which allowed much higher crystallization temperatures; fibres with moduli of up to 170 GPa and strength up to 5 GPa have been reported using this technique [25]. Both the "free-growth" and "surface-growth" methods will be described specifically in Section 5.) However, production rates for such extremely strong and stiff materials are very low. A subsequent development was direct spinning of UHMW–PE solutions followed by quenching and ultra-drawing of gel filaments. The fibres so produced can have moduli ~ 120 GPa and strength ~ 4 GPa, but most importantly can be produced at reasonable rates ($> 10\,\mathrm{m\,min^{-1}}$) [26–29]. It was soon recognized that the surface-growth method itself also proceeds by means of gel stretching at the rotor surface [30, 31].

Investigation of the various gels has led to the recognition of three distinct gel types, depending on the nature of the junctions in the gels listed in Section 2. One of these, the gel type with network junction zones made up of micellar crystals, has not yet to our knowledge been used purposefully to produce strong, stiff fibres. The second gel type forms on cooling dilute solutions of high molecular weight polymers which have been stirred. This is the type of gel which is built up at the rotor surface in the surface-growth apparatus of Zwijnenburg and Pennings [24]. The network junctions have high thermal stabilities, some persisting at temperatures above 130° C; however, we do not at present understand the physical nature of these junctions, except that they appear ultimately as fibrous crystals on further cooling. In the third case junctions are formed, or stabilized by, small lamellar single crystals [26]; this has led several groups to try to repeat the earlier single-crystal mat drawing work, but now using very much higher molecular weight polymers. Such experiments have produced fibres with moduli of ~ 200 GPa, although not as yet by a continuous production method.

We hope that we have managed to convey the main thread in the development of methods for producing strong, stiff fibres from solution. We shall now proceed to review each in technical detail.

4. Drawing single-crystal mats

4.1. Normal molecular weight polymers ($\bar{M}_w = 2 \times 10^4$ to 2×10^5)

The early work on drawing single-crystal mats used normal molecular weight polyethylene, and was chiefly concerned with morphology rather than mechanical behaviour. The principal observations of interest were that with a mat of sufficiently compacted single crystals a high draw ratio (~ 40) could be achieved, accompanied by a large increase in stiffness and strength. For example Statton [15] quotes a modulus of of 10.3 GPa and strength of 0.67 GPa for a single-crystal mat drawn by 40×. Maeda *et al.* [18] give a modulus of ~ 20 GPa and a strength of ~ 0.5 GPa for a draw ratio of ~ 23. High draw ratios can only be achieved using high drawing temperatures, typically 100 to 120° C; Statton [15] has noted that the drawability is improved by annealing (particularly under pressure) at ~ 125° C. A systematic study of the variation of modulus with draw ratio for single-crystal mats was carried out by Barham and Keller [19] using mats of Rigidex 50 ($M_w \sim 50\,000$, $M_n \sim 4\,000$). It was found that

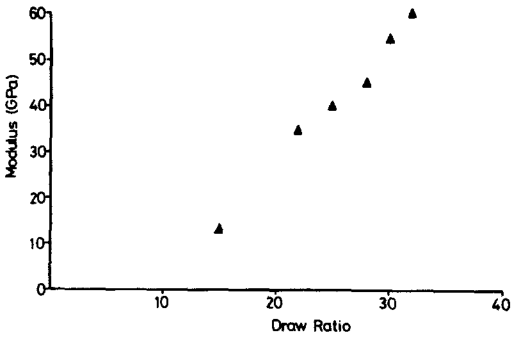


Figure 5 A graph of modulus against draw ratio for single-crystals mats of normal molecular weight polyethylene [19].

when drawing at temperatures between 90 and 110° C, draw ratios of up to 35 could be achieved; the modulus increased with the draw ratio as shown in Fig. 5.

More recently Kanamoto *et al.* [32] have used an extrusion technique to deform single-crystal mats where the mats are encapsulated within a split billet of polyethylene, the billet being extruded as a whole while in the solid state. In this way a single-crystal mat of a polymer of $M_w \sim 58\,000$ was extended to up to 45x at temperatures of 90 and 110° C. They were able to produce fibres with moduli as high as 60 GPa. They showed that the maximum modulus and draw ratio were higher for single-crystals mats than for spherulitic melt-crystallized samples of the polymer.

Most of these reports suggest that there is some significance in the fact that the maximum draw ratio which is achieved lies between 30 and 40. As already stated, in a single-crystal mat the chains lie perpendicular to the draw direction (Fig. 3b); if they are adjacently folded, the draw ratio to pull the folds out is L/a where L is the fold length of the crystal and a the spacing between chains along the fold plane. This ratio is typically expected to be 30 to 40. However, a recent investigation using neutron scattering from drawn single-crystal mats made of mixtures of hydrogenated and deuterated polyethylene [33] has shown that the actual molecular extension is very much less than the overall draw ratio. Thus we can now see that the draw ratio is not limited in this way, and that there must be some alternative explanation for the existence of a maximum achievable draw ratio of 30 to 40.

4.2. High molecular weight polyethylene ($\bar{M}_w > 5 \times 10^5$)

As a result of the recent gel-spinning experiments of Smith *et al.* [26] and Smith and Lemstra [27] interest in the drawing of single-crystal mats has revived recently, the new development being the use of ultra-high molecular weight polyethylene ($M_w \sim 10^6$) to prepare the mats. Kanamoto *et al.* [34] prepared single crystals from dilute solutions in xylene (0.05 and 0.2% wt %) by crystallizing for 20 h at 85° C; these were then slowly filtered out to form mats which were dried *in vacuo* at 50° C. The mats were drawn using a two-stage technique, the first stage involving use of the split billet extrusion technique at 110° C [32] to give a deformation ratio of 6 to 25. These fibres, which now had lengths between 3 and 10 mm, were drawn at a speed of 4 to 40 mm min^{-1} at a temperature between 20 and 130° C. A number of examples are quoted by the authors and are given here in Table II.

Note that very high draw ratios are reported; in particular a sample drawn at 115° C to a total draw ratio of 247 is quoted as having a modulus of 222 GPa. The authors found that their samples always broke at the grips at low strains and a stress of 1 to 2 GPa, so they do not make any claims about the ultimate strength of these fibres. However, a newspaper report from the group at Nara Women's College under Matsuo [35] quotes a strength of 5.9 GPa for a fibre drawn at 130° C to a draw ratio of 300. It is difficult to assess the morphology of the undrawn film, which is merely stated to have been made from a 0.4% solution of a polyethylene with $M_w = 4 \times 10^6$; however, we would expect this to be a single-crystal mat. More recently a third Japanese group, Furuhata *et al.* [36], have reported modulus against draw-ratio

TABLE II Tensile modulus of drawn UHMW–PE single-crystal mats (from Kanamoto *et al.* [34])

Draw temperature (° C)	Total draw ratio	Tensile modulus (GPa)
20	215	40
20	42	72
60	64	99
60	129	161
90	72	87
90	180	175
115	60	115
115	247	222
130	66	102
130	120	160

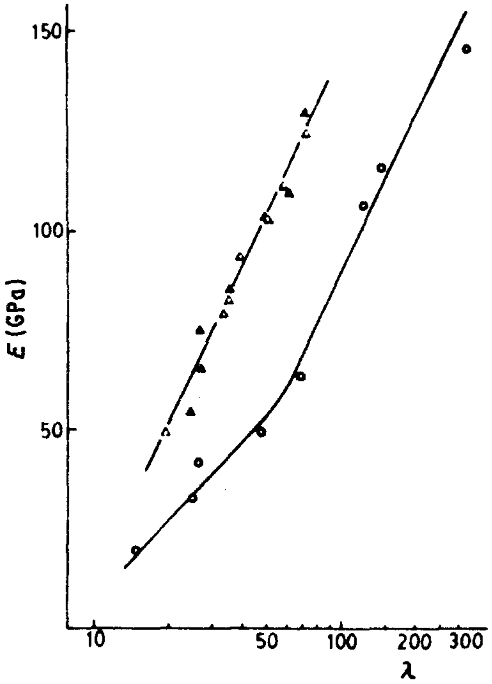


Figure 6 A graph of modulus E against draw ratio λ for single-crystal mats of two kinds of UHMW–PE. △ – Hizex 340 M, ○ – Hizex 240 M. From Furuhata *et al.* [36].

curves for the polyethylene Hizex (viscosity-average molecular weight $M_v = 1.55$ and 2.70×10^6) which we reproduce in Fig. 6; they find moduli up to 150 GPa and draw ratios up to 300.

There are still insufficient reports in the literature to draw many conclusions about the drawing of single crystals of high molecular weight polyethylene. However, several points are worth noting. It is clear that the maximum draw ratio (and modulus) which can be achieved increases with increasing molecular weight; this is in sharp contrast to the case of melt-crystallized material, where it decreases. Also it is clear that, just as for lower molecular weight polymers, the modulus increases with the draw ratio.

The early arguments that medium draw ratios of ~ 30 represent complete pulling out of folds in the single-crystal lamellae (Fig. 3) have been clearly demonstrated to be false both by the neutron scattering data, which show that the molecules deform very much less than the overall sample, and by the very much higher draw ratios which can be achieved when using high molecular weight polymers. In this context we would suggest that perhaps it would be more sensible to consider the maximum possible molecular extension in terms of the ratio of the overall molecular length to the size of chain in the single crystals before drawing. On this basis we would calculate (very approximately) maximum *molecular* extensibilities of ~ 50 for a molecular weight of 50 000, and ~ 500 for a molecular weight of ~ 2×10^6. Thus if we remember that the overall draw ratio is always larger than the molecular extension, we can see that we do not expect anything approaching full molecular extension to have occurred on drawing single-crystal mats.

5. Shish kebabs

5.1. General background

We shall briefly review the formation and structure of shish kebabs so as to provide an appreciation of developments in their production, and of their relation to strong, stiff fibres. We introduce the "crystallization thermometer" for the best-explored system of polyethylene in xylene solution (Fig. 7). Here the upper temperature limit for lamellar crystal formation T_{cr} is indicated. Below T_{cr} polyethylene precipitates as lamellae but above this temperature it stays in solution indefinitely.

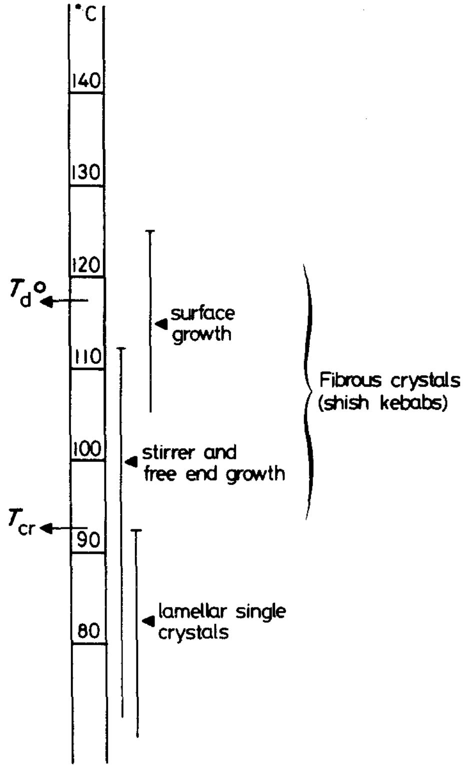


Figure 7 "Crystallization thermometer" showing the temperatures at which various types of crystallization can occur from xylene solutions of polyethylene. T_d^o is the equilibrium dissolution temperature and T_{cr} the upper limit for chain-folded crystallization.

It was found that in a limited temperature range above T_{cr} stirring the solution will produce a fibrous precipitate on the stirrer which consists of aggregated shish kebabs [14, 37]. This mode of crystallization is highly fractionating, the highest molecular weight end of a distribution being the most prone to form this fibrous precipitate [14].

The original explanation provided for this mode of crystallization was that the flow field produced by stirring extended the chains, such chain extension being more effective for longer molecules. The chains thus extended then crystallize in a fibrous form. Chains which had been left unextended, which comprise those below a certain chain length for a given stirring speed, use these preformed fibres (the shish) as nuclei for the deposition in the form of chain-folded lamellae, thus giving rise to the platelet overgrowths (kebabs).

The observation that these platelets formed on cooling the solution below T_{cr} suggested a method for eliminating platelet formation by filtration at the stirring temperature, thus removing the still uncrystallized chains. Alternately, as the platelet material was more soluble than the fibre, the platelets could be removed by heating the whole shish kebab aggregate to the original stirring temperature or above while still in the mother liquor. At an early stage of the subject it was claimed that totally smooth central fibres could be obtained in this way [38]. These claims proved to be erroneous. Indeed, large overgrowth platelets could be removed by high-temperature washing, or prevented by forming in the first place by hot filtration. However, the central fibre left behind was never smooth but contained smaller scale overgrowths, that is it was a shish kebab in itself [39]. We now introduce the distinction between macro- and micro-shish kebabs (Fig. 8). The platelets in the former are removable, for example by high-temperature washing, while in the latter they are permanent, indicating intimate molecular connectedness with an essentially extended chain core (Fig. 9). We shall be concerned with the latter micro-shish kebabs.

The modulus and strength of fibrous aggregates as peeled off the stirrer rod were measured and found to be higher than for conventionally drawn samples [10]. This was attributed to the presence of the central fibre, believed to consist of extended chains which should have extremely high modulus and strength. Accordingly, the overgrowth platelets were regarded as detrimental to the mechanical properties and efforts were concentrated on the reduction of the proportion of overgrowths. It was believed that the platelet-to-core ratio could be reduced by increasing the crystallization temperature, so that the chain-fold content would be suppressed. Indeed, both modulus and tensile strength were found to increase sharply as the crystallization temperature in the stirred solution was raised [10]. The highest temperature at which shish kebab crystals (micro-shish kebabs by the above definition) could still be grown was 113° C, and their modulus was 24 GPa. The fibres still showed appreciable platelet overgrowth, so there still appeared to be room for improvement. Eventually a new line of approach, the surface-growth method [23, 24], extended the temperature of crystallization up to as high as 126° C. The corresponding moduli increased dramatically, reaching a maximum of 150 GPa [40].

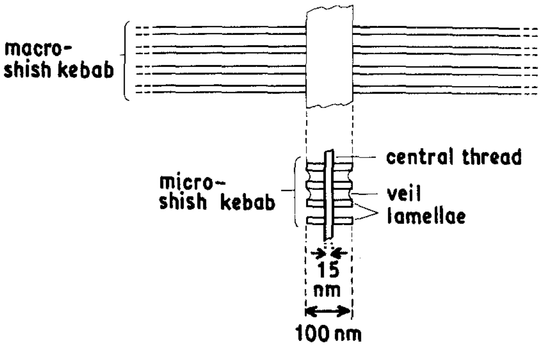


Figure 8 A sketch illustrating the difference between macro- and micro-shish kebabs. In the macro-shish kebabs the large platelets can be removed to reveal the central micro-shish kebab, whose platelets are intrinsically attached to the central thread.

5.2. The structure of shish kebabs

Before discussing these developments we must step back to Pennings' explanation [10] of the origin of the attached overgrowth (Fig. 9). Pennings

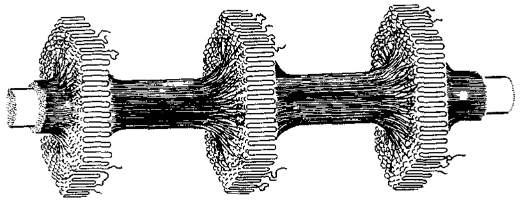


Figure 9 Schematic representation of a micro-shish kebab, indicating the intimate connectedness of the platelets with the central core (from Pennings [10]).

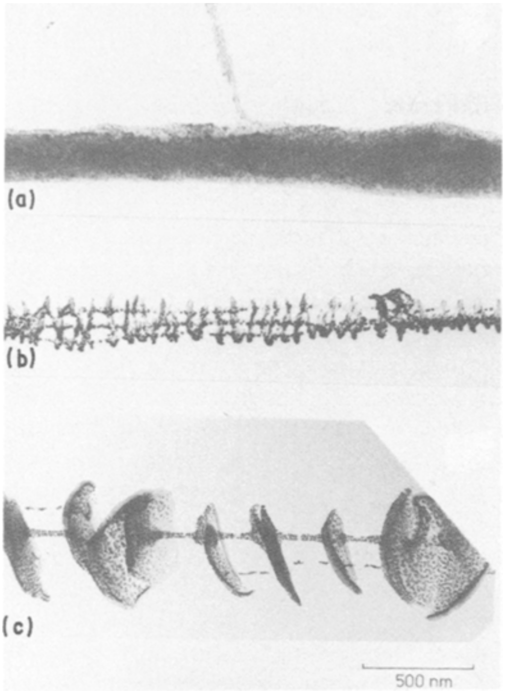


Figure 10 A series of electron micrographs demonstrating the three principal appearances which may be adopted by any shish kebab, depending on the way in which it is treated after its formation. The dark dots are gold particles used for decoration of certain features (from Hill *et al.* [41]).

noted that the size and spacing of the overgrowth platelets were affected by the way in which fibrous precipitate (once formed) was cooled, and by the length of time it was stored at some elevated temperature before final cooling [22]. Further, the size of the overgrowth platelets and the spacing between them, once developed, could be altered by subsequent storage at appropriate elevated temperatures below the temperature of the original fibre formation (T_f). It was concluded that the fibres when formed are "hairy", and it is these attached (but loose) hairs freely dangling in solution which crystallize in a chain-folded manner at a lower temperature during cooling, the precise size and spacing of the overgrowths being influenced by the cooling conditions.

The latest observations [41] reveal that the same applied even to smooth fibres. Smooth fibres can, by appropriate storage treatment, be converted into micro-shish kebabs, and micro-shish kebabs into smooth fibres. This means that all fibres are initially formed "hairy", and dependent on cooling conditions the hairs may form as chain-folded platelets or a structureless sheath; the different appearances are mutually intra-convertible. It follows that the external appearance is merely "hairdressing". This is illustrated by Fig. 10, where we show a series of micrographs of the appearance of a single preparation as we vary the storage and cooling conditions. The modulus and strength of the fibres (at least when measured at room temperature) are independent of the appearance of the overgrowth; they depend only on the initial formation temperature [41], as shown in Fig. 11. Thus while we see that the mechanical properties are improved by increasing the shish kebab core-formation temperature T_f, we also see that this is not due to a change in the platelet-to-core ratio. It is the structure of the cores themselves which is important. In the first instance the cores were envisaged as more or less continuous extended-chain crystal. In the light of recent results this does not appear to be tenable. The core is envisaged rather as an assembly of elongated bundle-like crystals of finite length, connected by fringe-like oriented

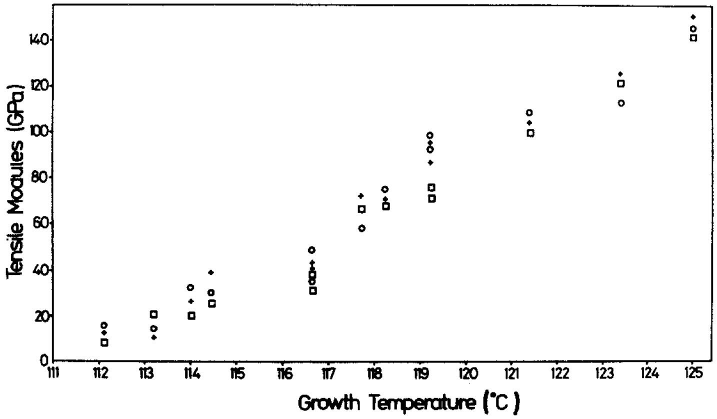


Figure 11 A graph showing that the tensile modulus of shish kebab fibres depends only on the growth temperature of the shish kebabs and not on their physical appearance, which is merely "hairdressing". The different symbols refer to the different morphologies seen in Fig. 10 (from Hill *et al.* [41]).

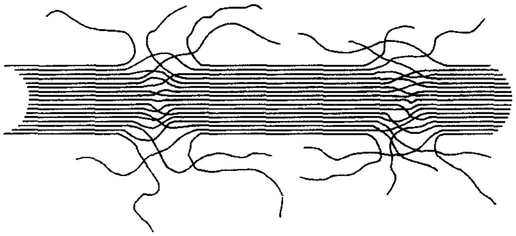


Figure 12 A sketch illustrating our current views of the structure of the central core of a shish kebab. Elongated bundle-like crystals are connected by fringe-like amorphous regions. The chains emanating from these regions crystallize later to form the platelets. The ends of the crystals are shown tapered to allow for the lower density of the amorphous regions.

amorphous regions (Fig. 12). This picture has emerged from the study of thermal behaviour [42].

The gradual shrinkage of the fibres on heating can best be interpreted as progressive melting of increasingly longer crystals; the actual length distribution of crystal bundles can be deduced. The mean crystal length is found to increase with T_f [43], and this must be responsible for the corresponding increase in modulus with increasing T_f. Thus we arrive at the model of a fibrous composite where the crystallites act as reinforcing agents of finite length. The effectiveness of such a reinforcing element increases with its length. This is readily treated by composite mechanics, and such a treatment can give reasonable agreement between the moduli calculated from the lengths of crystalline segments measured by thermal shrinkage and their actual measured moduli. We can account for the increase in modulus with formation temperature not in terms of a decrease in platelet-to-core ratio, but instead in terms of the observed increase in length of crystalline regions in the cores [43]. An alternative explanation has been proposed by Grubb [44] using a simple composite model with more- and less-compliant regions corresponding to amorphous and crystalline segments of the fibrous core respectively; the segments are coupled in series, and it is assumed that the ratio of the lengths of the crystalline and amorphous zones in the central core varies with T_f.

5.3. Formation of shish kebabs

Shish kebab crystals are formed by stretching and subsequently crystallizing chains. The high extension necessary is much larger than that observed in traditional flow-birefringence studies in simple shearing flows. Shish kebabs are formed only when the stirring is so vigorous that vortices are produced. These do not arise at low stirring speeds, where only a simple shear flow field is generated. It is the extensional flow between counter-rotating vortices which gives rise to the high chain extensions needed for shish kebab formation. Such flows stretch out rather than rotate a given fluid element. If such a fluid element contains a dissolved macromolecule, the chain will extend. Longer molecules are more readily extended, which may explain the observed preference of the higher molecular weights to form shish kebabs [45]. These observations focused attention on elongational flow, and provided the impetus for systematic studies of chain elongation.

Elongational flow is a common feature of all flows passing through a constriction, and it occurs in all spinning processes. In traditional spinning, however, full chain extension is not achieved; the strain rates are usually not high enough, and the solid walls of the spinnerets create transverse velocity gradients in their vicinity. This results in dominantly simple shear flow, with only modest chain-aligning properties. Systematic elongational flow-works utilize systems which create high and (for simplicity) uniform acceleration of the flow, without the presence of solid walls. The simplest of these has been the double suck-jet [45]. Complete chain alignment and extension of solute molecules can be achieved between the jets along the jet axis, verifying predictions from solution hydrodynamics. Further, when conditions are inducive to crystallization (such as for polyethylene at sufficiently low temperatures), shish kebab fibres may be produced in the corresponding localities between the jets.

Once shish kebabs have formed they influence the flow field around them in a way which promotes chain alignment and further growth. By forming an obstacle within the flowing solution they give rise to a stagnation point (a locality of zero velocity) behind their downstream tip. As the flow will have to reach the velocity of the surrounding medium downstream from this stagnation point, it will have to accelerate along a straight line away from the fibre tip [46]. The flow will be elongational, creating favourable conditions for continued fibre growth. This applies irrespective of the nature of the overall

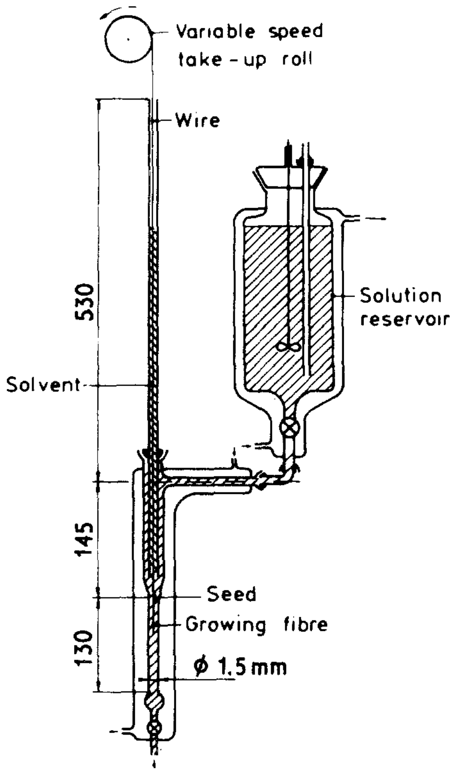


Figure 13 The apparatus used by Zwijnenberg and Pennings [21] to produce continuous shish kebab fibres by the technique which has become known as the "free-growth" method.

flow field: a fibre immersed in a uniform flow field (that is, with no velocity gradient) will create its own elongational flow at the immediate vicinity of its tip.

5.4. Methods of shish kebab production

We may now see that practical requirements for fibre production include the need to produce continuously a parallel assembly of shish kebabs formed at temperatures (T_f) as high as possible.

These requirements were first achieved by the so-called "free-growth" method. A seed fibre, obtained separately (it could even be a foreign fibre, say cotton) was immersed in a flowing solution at a temperature above T_{cr} (see Fig. 7) and withdrawn in opposition to the flow (Fig. 13) [21]. Here the fibre grew at the tip, and a steady state could be reached where the growing fibre tip always stayed at the same position while being wound up at the other end. This free tip-growth method was readily explained by self-generated extensional flow at the fibre tip, as predicted by the fundamental considerations outlined above. The mechanical properties, while appreciable, were still further from the theoretical than could have been wished.

Higher values of T_f were realized rather unexpectedly by the "surface-growth" method [23, 24]. Here a seed fibre was immersed in a solution between two concentric cylinders where the inner one was in a state of uniform rotation, the solution temperature again being above T_{cr}. It was found that when the tip of the seed fibre contacted the rotating cylinder it "hooked" on to it, so that it could be pulled without the tip becoming detached. What follows this attachment is quite unexpected. The fibre grows from the tip at the point of attachment to the rotating cylinder. By winding up at the far end on a bobbin, and by replenishing the solution in the gap between the rotor and the stationary vessel, a fibre can be produced in a continuous fashion (Fig. 14). There seems to be no limit to the length: bobbins of many kilometres can be wound up at rates of up to $3\,\mathrm{m\,min^{-1}}$. It was found that T_f could be raised higher than was possible before, in fact beyond what was believed to be the equilibrium dissolution temperature (the theoretical maximum)

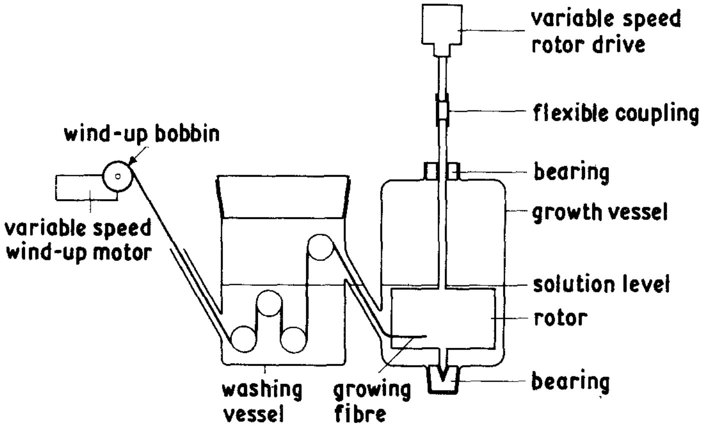
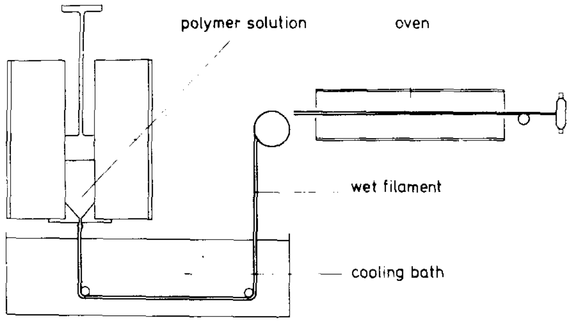


Figure 14 The apparatus we have used [40] to produce continuous fibres of high stiffness and strength by the surface-growth method of Zwijnenberg and Pennings [24].



Schematic representation of the solution spinning/drawing process.

Figure 15 The gel spinning apparatus used by Smith and Lemstra [27]. The hot polymer solution is extruded into the cooling bath where it forms a gel filament; this wet filament then passes into the air oven where it is heated and stretched to form the high-strength, high-stiffness fibre.

for polyethylene, with an accompanying rise in modulus and tensile strength. Thus a modulus of 100 GPa and tensile strength of 2.5 GPa could routinely be achieved at $T_f = 121^\circ$ C, and 150 and 4.5 GPa respectively at $T_f = 126^\circ$ C [40]. For a given T_f the different variables (rotor speed, take-off speed and solution concentration) could be optimized. The basis of a novel method for ultra-high modulus fibre production has thus been laid. We should, however, add one cautionary note here. Although very strong and stiff fibres can be produced at high temperatures, the rate at which they can be made is comparatively low. The maximum production speeds decrease as the temperature (and modulus) increase.

The maximum production rate at a given T_f can be increased a little by deliberately moving the growing fibre up and down the rotor surface [25]. Alternatively, several fibres may be grown simultaneously on the same rotor as shown by Sapsford and Mackley [47]. Kavesh *et al.* [48] have also grown several fibres at the same time using a somewhat modified arrangement where a polytetrafluorethylene surface is kept stationary and the growing fibres are pulled around it. However, in all these cases the rates were low compared with those in commercial fibre-spinning methods.

The new surface-growth method brought new elements into the underlying scientific picture. From the structural point of view the picture was still unaltered. The higher T_f achieved seemed to reduce the kebab (platelet) content of the shish kebab, provided the fibre was led through a washing bath which prevented the formation of large platelets depositing from the solution; in fact for the highest T_f values (above 119° C) entirely smooth fibres were claimed. However, we now know that the smooth appearance is the result not of the high T_f but of the subsequent cooling conditions. The quite unexpected new element, however, has been the influence of the solid rotor surface. The notion has arisen that a layer of polymer adsorbs on to the rotor and enmeshes with the hairs emanating from seed crystals in contact with it, enabling the latter to support loads. The whole enmeshed assembly is then stretched, leading to stress-induced crystallization at the fibre tip at the surprisingly high temperatures in question (Fig. 7), somewhat in the way envisaged in Fig. 16 (Section 6). The fibre tip grazes the rotor surface, depleting from it the adsorbed layer as it grows; this layer is then replenished through new molecules arriving from the solution. Clearly a single molecular adsorption layer will not provide a sufficiently large supply of material for the growth to proceed. Consequently a multimolecular layer, a so-called entanglement layer, has to be invoked [30].

At this point the following needs to be noted. Elongational flow as a direct cause of fibre formation, while not discarded, has been relegated into a rather unspecified backgroud role; the importance of solid surfaces and adsorption has now come to the forefront.

6. Gel drawing

6.1. Background

Our own interest in gels and gel spinning follows from the recognition that the shish kebab fibres produced by the surface-growth method are produced by the deformation of a gel-like entanglement–adsorption layer at the rotor surface [30, 31]. This has led us to the study of methods of formation and subsequent drawing of gels. Several continuous processes for the production of strong, stiff fibres which allow direct production by stretching of gels at quite respectable rates have been reported. We show in Fig. 15 the equipment used by Smith and Lemstra [27]. All these processes start by making a gel from the polymer solution and then deforming the gel before, during, or after removal of the solvent. (The main steps, as related to the type of apparatus shown, are indicated in the caption to Fig. 15.) We believe that all these processes are essentially similar, the various methods of solvent extraction and drawing serving more to make production of fibres easier with a given piece of apparatus than to distinguish between fundamentally different processes. However, within the gel itself before deformation there can be fundamental differences in structure.

6.2. Classification of gel types

The existence of different classes of gel, as distinguished by the nature of the network junctions, has been indicated in the introductory and historical parts of this review. At this point the subject will be treated in more specific detail.

6.2.1. Method of classification

Three distinct classes of thermoreversible gel can be produced from solutions of crystallizable polymers [49], distinguished by the temperatures at which the gels form on cooling and melt on subsequent heating. This can be very simply expressed in terms of the gel melting temperature, both in absolute terms and (more conveniently) relative to the temperatures where the system becomes turbid on cooling, or clears on heating; the appearance of turbidity corresponds to the formation of lamellar single crystals, and the clearing to their dissolution. The least stable gels (Class I) will always melt at a temperature below the solution clearing temperature, leaving a turbid but fluid suspension; it is in such gels that the junctions forming the network are believed to be of a micellar nature (Fig. 4). The most stable gels (Class II) melt at a temperature above the solution clearing temperature. These gels are formed from solutions such as those that have first been stirred at high temperatures (above the dissolution temperature of the polymer) and subsequently cooled. Such gels melt well above the equilibrium temperature for the polymer crystals. While we have some speculative ideas, we do not know what forms the very stable junctions in these gels. We do know for certain that they reveal fibrous elements and shish kebabs when examined after cooling (a necessary step for such an examination), the nature of the gel at the formation temperature itself being inaccessible at present. The third class of gel (Class III) melts at the solution clearing temperature itself; in this case the network junctions are either the lamellar single crystals themselves, or entanglements between molecules still in solution which are stabilized by the crystals.

All three classes of gelation have been observed in polyethylene, although Class I (micellar junctions) has only been seen in low molecular weight material at very high concentrations of ~ 8% [50]. Classes II and III are observed in high molecular weight polyethylene, and both have been used to produce strong, stiff fibres. In the present fluid state of the subject this distinction between different classes of gel is not generally recognized, and it is often not clear from the literature which one is involved in a given piece of work. In what follows we shall attempt to deduce this, either from first-hand knowledge or by relying on our general experience in the subject.

We ourselves [41, 43] have used the thermally most stable type (stirred gels, Class II) while Smith and Lemstra [51–54] have used the next most stable class (single-crystal gels, Class III). The original paper on gel spinning by Smith *et al.* [26] does not specify which type of gel was used. Subsequently Pennings and co-workers [28, 55–60] and Smith and Lemstra [27, 54] have developed separate techniques and processes. There are several other reports of gel drawing processes [16, 29, 61–63] where we have no indication as to which types of gel was used, although we expect mixtures of Types II and III.

In what follows we shall start by describing the classification of gel types, and then proceed to show how these can be used as precursors to produce strong, stiff fibres; we shall follow this by outlining the principal methods of gel drawing. Before proceeding, however, the following needs stating. The distinction between gel classes is highly significant for the purpose of acquiring fundamental knowledge, in particular that of crystallization, associative behaviour, entanglements, adsorbtion, and flow-induced chain extension of polymeric systems. However, it is only of secondary significance for the purpose of producing ultra-stiff and strong fibres. Once a gel of suitable drawing characteristics is produced it is of no primary consequence for fibre production what the nature of the junction is, and how the gel has arisen. The essential point is that gel structures allow the attainment of high draw ratios, which is the key to favourable properties.

Wherever this alone is of consequence, gels merely serve as a means to an end.

Having presented a general survey of the various gel types we shall now give a more detailed discussion of individual gel classes. This is designed to serve two purposes. The first is to give more specific information on how the gels currently used in fibre production arise, for those readers who may be interested in gels for their own sake. (For a more explicit survey on thermoreversible gelation as such, we refer to an earlier review by one of us [49], recognizing that some changes have taken place since then). The second purpose of the following sections, including that on the survey of spinning techniques, is to help those who may require clarification regarding the nature, identity and/or difference between the different reports and claims featuring in the literature (including patents) on gel spinning. We recognize that some of the detailed particulars serving this latter purpose may present problems to the uninvolved reader seeking general informaion only: he is either referred to the original references quoted for fuller comprehension and appreciation, or encouraged to skip the appropriate sections according to interest.

Before embarking on specifics a further general statement is needed. Polyethylene dissolves only at elevated temperatures. In the course of all the treatments to be described the solution is cooled to room temperature at one stage or another. In the course of this, lamellar crystals of the kind shown in Fig. 3 will form. Such crystals will therefore always be present in the final product, and in fact will represent the majority of the final precipitate. They will impart turbidity to the suspension or gel; the appearance of this turbidity on cooling is an indicator of their formation, and the clearing of the system an indicator of their dissolution.

The platelet crystals thus identified can have different functions according to the class of gelation; and even in each class, they can be in different forms in relation to the system. In Class III (single-crystal) gels they form the junctions themselves. Inevitably there will be platelet crystals even in this class which will not be load-bearing, and may only be loosely-connected or isolated occlusions arising after the gel has already formed. In pure Class II (stirring-induced) gels the platelet crystals are always incidental, and do not contribute to gel formation. They can be present as overgrowth crystals (kebabs) on the fibrous crystal cores, which themselves may or may not be junction-forming. In addition they will be present also as loosely connected or totally isolated occlusions, just as in the case of the single crystal (Class III) gels. In both classes, in whatever form present, they will contribute to the turbidity of the system. Furthermore, they will always represent the majority component of polymer present, irrespective of whether they contribute to the network or not. The latter is a very important point, because it implies that when the network is drawn out such platelet crystals are necessarily extended with it. Conversely, if we are to have a drawn fibre which consists predominantly of extended chains, the majority of the latter must arise from the chain-folded crystal, irrespective of the part played by these platelets in the network structure.

6.2.2. Stirring-induced gels (Class II)

We recognized that dilute solutions (< 0.1 wt %) of ultra-high molecular weight polyethylene, such as those used for surface-growth fibre production, were prone to gel on cooling in the quiescent state following agitation at temperatures too high for normal crystallization [31]. Let us look again at the "thermometer" in Fig. 7. At (say) 135° C, absolutely nothing normally happens, and there are no visible changes on agitation at that temperature. However, if the solution is cooled after the agitation is stopped, it sets as a transparent gel at a temperature of about 100° C in the quiescent state. On further cooling this gel becomes turbid owing to the usual precipitation of lamellar crystals. We have shown that only solutions which gel in the above manner can support fibre growth by the surface-growth method, as in Fig. 16 [31]. The implication is that in the surface-growth method the fibre is actually produced from a gel. The building up of an adsorption entanglement (or gel) layer at the rotor surface has been directly observed [31, 64, 65]. It is well known that stretching of networks is one way of producing shish kebabs [66]. It emerges therefore that shish kebabs arising by these methods are formed by the stretching of gel networks, rather than through crystallization of individually extended separate molecules as previously envisaged.

We have made gels in this way [43] by stirring dilute solutions (0.75 wt %) of Hostalen GUR (Hoecht, W. Germany) ($M_w \sim 1.5 \times 10^6$) for 10 min at 115° C. The solutions were then allowed

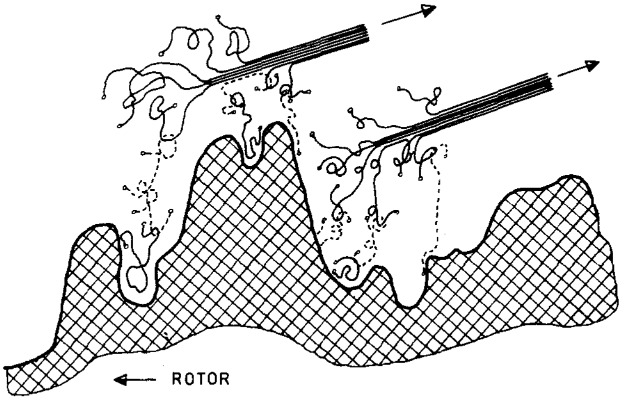


Figure 16 Diagram indicating how the surface-growth process may occur (from Zwijnenburg [23]).

to cool, and formed clear gels at ~ 100° C; on further cooling below ~ 70° C the gels become turbid. Strips of these gels were reheated while surrounded by solvent, and drawn at various temperatures up to ~ 120° C at 45 cm min^{-1} to produce fibres. Most of the solvent was expelled from the fibres during drawing. We found (Fig. 17 and [43]) that the modulus of the dried fibres increased with draw ratio, and that the modulus at the maximum draw ratio increased with drawing temperature (Fig. 18). Indeed, in a parallel series of experiments we found (by using the technique of Fig. 14) that the maximum modulus of drawn gel fibres corresponds very closely with the modulus of surface-grown fibres prepared at the same temperature. We also showed that the morphology of these fibres was identical to that of surface-grown fibres; they both consisted of array of shish kebabs.

If the gels are dried before drawing either by soxhlet extraction (which tends to leave a highly porous, low bulk density product), or by the use of pressure to expel solvent, or simply by allowing the solvent to evaporate, then the solid products are still highly extensible. At temperatures of ~ 100° C draw ratios of up to ~ 100 can be achieved [43]. The modulus and strength of the fibres increase with draw ratio. The function of the drawing temperature is indirect, in as far as higher drawing temperatures enable the attainment of higher draw ratios. However, if the temperature becomes too high (> 130° C) then this increase in draw ratio becomes less effective in enhancing the modulus, as the material begins to undergo viscous flow. A model which explains qualitatively the variation of modulus with drawing temperature of the wet gels using composite mechanics has been proposed [43]. The lengths of the mechanically coherent crystalline regions in the shish kebab backbones will increase with the formation temperature T_f [42, 67]. According to our own model at least, this improves the ability of these crystals to transfer stress by shear through the remaining material.

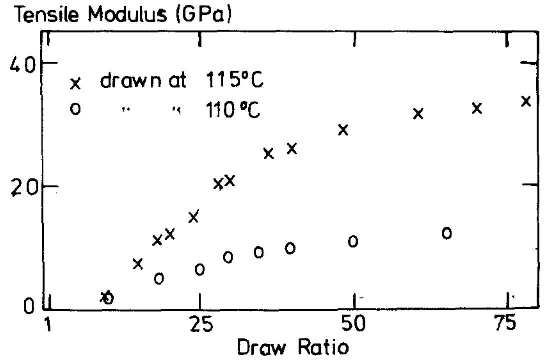


Figure 17 Tensile modulus of wet-drawn gel fibres (measured after drying) as a function of draw ratio. From Barham [43].

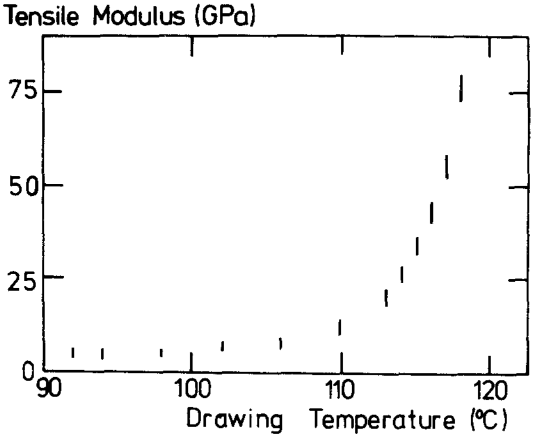


Figure 18 Maximum tensile modulus of fully wet-drawn gel fibres as a function of the drawing temperature. From Barham [43].

6.2.3. Single-crystal gels (Class III)

This type of gelation occurs on cooling unstirred solutions of high molecular weight polyethylene. One significant difference as compared to Class II gels is that the concentrations required are much greater than those for the stirred gels, e.g. for a molecular weight of $\sim 1.2 \times 10^6$ a minimum concentration of ~ 1% is required before gelation will occur, rather than precipitation of individual single crystals (compare the concentration of 0.1% for Class II stirring-induced gels). This class of gels, if left to dry, has a morphology (as identified by low- and wide-angle X-ray diffraction) that is very similar to single-crystal mats [68]. On small deformation of wet gels, the crystals align with their long axes parallel to the draw direction, i.e. with the crystallographic *c*-axis normal to the draw direction [49, 69]. Such unusual orientation effects in the intermediate stages of stretching do not occur to the same extent when drawing the stirring-induced gels; indeed it is possible to draw such Class II gels at higher temperatures in the absence of any lamellar single crystals.

6.3. Extending the gels

The gel spinning process may be conveniently divided into two parts: firstly the preparation of a substantially unoriented gel filament, and secondly the processing of this filament to form a highly oriented strong, stiff fibre. These processes will be briefly described with some further details in the Appendix. In describing the subsequent drawing process, particular attention will be paid to the dependence of the modulus on the draw ratio. For this latter purpose we shall draw primarily on some work of Smith and co-workers [51–54], in which they used what we consider to be essentially single-crystal (Class III) gels.

Pennings and co-workers [28, 55–60] have prepared gel fibres by spinning a solution at 170° C (using paraffin oil as the solvent) through a long, conical die. The filaments are quenched by the surrounding air as they leave the spinnaret, and during this quenching a gel is formed. Prior to hot-drawing the solvent is extracted in *n*-hexane and the fibres dried in vacuo. Smith and Lemstra [27] have also used a continuous process (illustrated in Fig. 15) in which a hot decalin solution is spun into a cold-water bath, where it forms a gel which may then be drawn in an air oven. Both these techniques use comparatively concentrated solutions which are quenched, so we expect that the gels will be predominantly of Class III; however, the solutions will have undergone considerable shearing during the spinning process so that we may expect some Class II gelation to have occurred as well.

In a separate study Smith and co-workers [51–53] have prepared gel fibres by casting the hot decalin solutions into trays where, on cooling, a gel forms. In these cases, where no shearing is involved, we expect the gel to be purely of Class III.

Turning now to the stretching of the gels to form strong, stiff fibres, there are two cases to be noted: stretching before, and after, removal of the solvent. Examples for each are given by the work of Smith and co-workers [51–54]. In both cases it was found that both the modulus and strength increased to up to ~ 120 GPa and 3 GPa respectively at draw ratios of > 30, using a polymer of $M_w \sim 1.2 \times 10^6$. In the case of the gels drawn while still wet, drawing was conducted in an air oven so that the solvent was evaporating at the same time as the gel was being stretched. which makes interpretation difficult. There is however a remarkable difference in maximum drawability between what are referred to as dilute solutions – those containing ~ 2 wt % of polymer, where draw ratios in excess of 30 are easily achieved – and "concentrated solutions" – those containing up to 50 wt % of solvent – where the maximum draw ratio was found to be ~ 5, i.e. much the same as for melt-crystallized material. The same authors have also shown (Fig. 19) that the dependence of modulus on draw ratio is essentially independent of the temperature of drawing. The maximum draw ratio, and hence maximum modulus, was highest at an air temperature of ~ 110° C, i.e. around the dissolution temperature of the single crystals. Drawing at higher temperatures was possible, but samples failed at lower draw ratios.

The dried gel films in the experiments of Smith *et al.* [51] and Smith and Lemstra [52] were prepared by allowing the solvents to evaporate, removing the last traces of solvent by washing with hexane or ethanol. They found distinct variation in the drawing behaviour of these dried gels, both with initial gel concentration and drawing temperature. This is illustrated in Fig. 20, where the maximum extensibility is plotted as a function of the initial gel

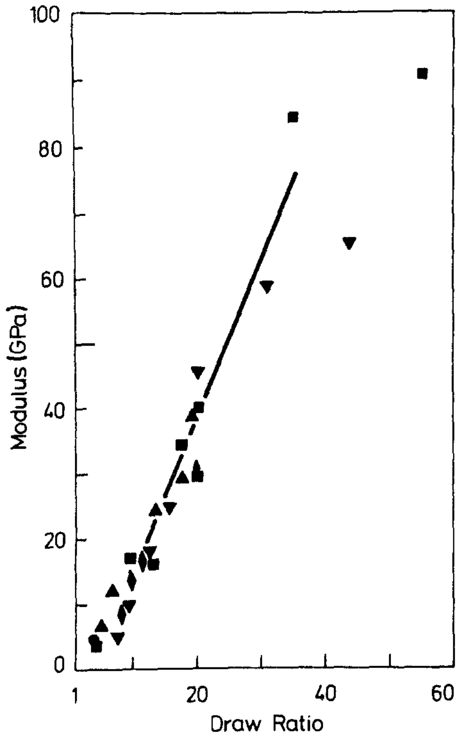


Figure 19 Tensile modulus of drawn, initially wet, single-crystal gel fibres as a function of draw ratio. Different symbols indicate different drawing temperatures. From Smith and Lemstra [52].

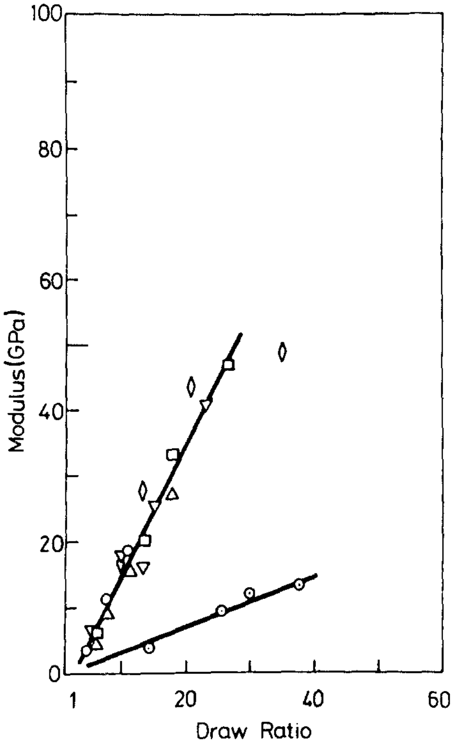


Figure 21 Tensile modulus as a function of draw ratio for dried single-crystal gel films. The different symbols refer to different temperatures: ○ – 70° C; △ – 93° C; □ – 106° C; △ – 120° C; ◇ – 133° C; ⊙ – 143° C. From Smith and Lemstra [52].

concentration. In particular they found, as for the wet gels, that the modulus increased with draw ratio and that, provided the drawing temperature was less than ~ 135° C, the relation between modulus and draw ratio was independent of the temperature of drawing (Fig. 21). At higher draw temperatures, although the maximum achievable draw ratio continued to rise, the modulus increased more slowly with increasing draw ratio (the line with the lower slope in Fig. 21).

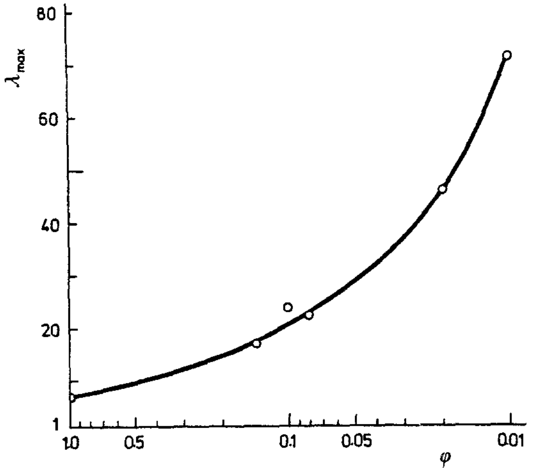


Figure 20 The maximum extensibility λ, of dry single crystal gel films as a function of the initial gel concentration φ (% w/v), from Smith *et al.* [53].

Most significantly, in the same study of dried gel films [53] it was found that the maximum draw ratio at a particular temperature increased with concentration (C) as $C^{-0.5}$, and from this it was deduced that the drawability is controlled by the number of entanglements present in the gel. If there are only few entanglements present (as may be expected at low concentration) then the extensibility is high. If the system is taken to be a simple network it is then easy to show that $\lambda_{max} \propto C^{-0.5}$. Since we are dealing here with dry gel films in which the crystallinity is comparatively high (~ 50%), the crystals themselves must be quite plastic and do not limit the drawability. In other words, the maximum achievable draw ratio in a dry gel film is determined solely by the degree of entanglement (and hence concentration) in the original gel. Thus the crystals, in whatever form they are contained, must be highly ductile at the draw temperature.

7. Evaluation of methods

The recent development of methods involving gelation to produce strong, stiff polyethylene fibres has its roots in the surface-growth technique [23, 24, 70] rather than in earlier gel-spinning work using lower molecular weight polymers [16, 61–63]; the latter will be referred to more explicitly in the Appendix.

There have been essentially three approaches. At Bristol our objectives were to understand the underlying mechanisms of the surface-growth technique; this led us to the identification of absorbtion–entanglement layers [64] and to the discovery of stirring-induced gelation [31]. Our chief objective in preparing and drawing gel fibres [41, 43] was to demonstrate the equivalence of gel drawing and surface growth. These studies showed, amongst others, that the drawn gel fibres (like the surface-grown fibres) consist of parallel arrays of shish kebabs, and have led us to speculate on the nature and formation of shish kebabs themselves.

Developments in the Netherlands have led to the same recognition, namely that gel spinning gives rise to strong, stiff fibres [26, 71, 72]. Smith *et al.* [53] emphasized the importance of entanglements for the drawability of their single-crystal gels (Class III by our classification). Meanwhile Kalb and Pennings [55] at first emphasized the porosity of their fibres, and aimed to explain the drawability in terms of free-volume effects. Subsequently, however, work from the same laboratory, (Smook *et al.* [56, 57]) suggested that the high extensibility is due to low entanglement density, the importance of porosity (if any) being restricted to its effect on such properties as heat transfer during drawing.

In the USA, Kavesh and Prevorsek [29] have lately developed a more complex process involving solvent exchange, in which they have attempted to characterize their material before drawing in terms of its porosity.

The common factor in all these methods is the gel itself, which irrespective of whether still wet or already dried contains significantly fewer entanglements than its melt-crystallized counterpart. This allows the attainment of much higher draw ratios, leading to higher chain extensions which in turn promote high stiffness and strength.

A more academic consequence of the new recognition relates to current ideas on the origin of shish kebab crystals. Stretching of networks or gels is, as we mentioned previously, a method for producing shish kebabs. Indeed we are coming to believe that most, if not all, shish kebabs reported in the literature were formed by the stretching of gels; if not by stretching of macroscopic gels as in our own recent work [43] and in the surface-growth method, then by stretching small gel-like particles of highly entangled molecules. Thus the formation of shish kebabs from isolated molecules, previously held as a universal method, still awaits verification.

We believe that whenever molecules (or networks of molecules) which are essentially in solution are stretched, as in the hot drawing of wet gels, then shish kebabs are produced. Once the chains are locally all extended and aligned they will crystallize together to form shish kebab cores. In our opinion this applies not only to our own work using stirring-induced gelation but also to the gel-drawing work of others, in those cases where the gels are drawn in the presence of solvent at temperatures above the dissolution temperature of single crystals (i.e. above ~ 110° C; see temperature scale of Fig. 7).

On the other hand gels which have been cooled to room temperature and dried thereafter consist essentially of single crystals, and hence have a morphology similar to that of a single-crystal mat. This is true not only of the single crystal but also of the stirring-induced gels. In this case we believe that the increase of modulus with draw ratio is determined by the deformation behaviour of the single crystals, rather than by any property of the original gel. The importance of the original gel state lies in the fact that it allows the attainment of very high draw ratios (and correspondingly high moduli) due to the intrinsically loose load-bearing network structure it represents; the maximum attainable draw ratio and modulus are determined by the underlying entanglement density in the fashion laid out above.

We can best illustrate these contentions by plotting on a single graph all the previously mentioned modulus and draw-ratio data for drawing temperatures below 120° C, both for single mats and dried gels. This has been done in Fig. 22. It is clear that there is a more or less unique relation between modulus and draw ratio, higher draw ratios giving higher moduli. This relation is independent of molecular weight and the nature of the undrawn material. Nevertheless the maximum

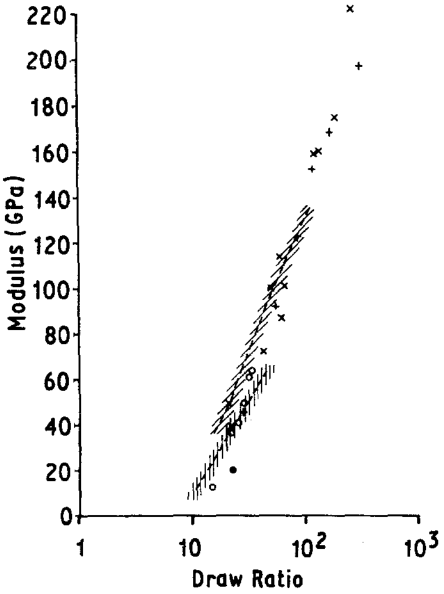


Figure 22 Tensile modulus against draw ratio of dry gel films and single-crystal mats. The line with the vertical hatching refers to gels and is from Smith and Lemstra [52]; that with horizontal hatching to single-crystal mats from Furahata, Yokokawa and Miyasaka [36]; from Kanamoto, Sherman and Porter [32]; (o) from drawing normal molecular weight single-crystal mats [15, 17–19]; (+) from drawing high molecular weight single-crystal mats [50].

draw ratio which can be achieved does depend on the initial sample. In case of gels (e.g. Fig. 20 relating to dried gels) it increases with decreasing initial solution concentration. In the case of single-crystal mats it also increases with increasing molecular weight.

As an additional point of important practical consequence it needs stating that though the short-term mechanical properties like modulus and tensile strength are shown to be independent of the production technique, there are large differences in the long-term properties, notably creep [29]. Surface-grown fibres show a much higher creep rate compared with gel-spun fibres produced from the same polymer.

In summary, we can now see that there are only two mechanisms leading to strong, stiff fibres. Firstly, we can crystallize pre-aligned chains as shish kebabs by stretching uncrystallized networks of polymer chains. This mechanism occurs in the free-growth method of Zwijnenburg and Pennings [21], in the surface-growth method [23–25], and in our hot drawing of wet, stirring-induced gels [43], i.e. at temperatures above which single crystals can form or survive.

The other mechanism is the large-scale deformation in the solid state of polymer single crystals. This occurs in the drawing of all gels in which single crystals have been allowed to develop and have been retained up to the stage of drawing; this includes all cases of drawing dried gels, whether of stirring-induced or single-crystal type. It also includes the drawing of single-crystal mats as obtained from suspensions (i.e. without explicitly involving gels).

We may further expect that in those processes where wet gel fibres are drawn in an air oven, so that solvent evaporates during drawing, a combination of these two mechanisms will operate.

8. Concluding remarks

We have seen that by dissolving high molecular weight polyethylene and then (by whatever means) producing a gel, a network may be formed which is only loosely entangled. This network may then be stretched to high extensions and gives rise to strong, stiff fibres. Furthermore, we have seen that irrespective of whether the solvent is removed or not the resulting platelet crystals, which are the representative components of the gel after cooling to room temperature (or after solvent removal at any temperature below the melting point) are themselves highly plastic; they can be stretched to very high draw ratios, again leading to strong, stiff fibres. We started by classifying the routes to strong fibres: drawing of single-crystal mats, direct production of shish kebabs, and gel spinning; we hope that we have shown that all these three are closely interrelated. The usual shish kebabs as obtained by present practice are probably the result of stretching gels on a localized scale, rather than (as previously believed) individual chains. Indeed it is well known that shish kebabs are produced when a swollen network obtained by prior chemical crosslinking is stretched at temperatures otherwise appropriate for shish kebab formation.

Single-crystal mats made from dilute solutions of high molecular weight polymers are extremely ductile at elevated temperatures, and the best properties so far achieved have come from the hot drawing of such mats. When gels are allowed to cool and dry out slowly they form materials which have a texture very similar to single-crystal mats, and on drawing also give very strong, stiff fibres although the attainable maximum draw ratios (and hence modulus and strength) decrease with an increase of the initial solution concentration. It is such gels which are being used in the various continuous production methods. Here the gel is obtained first in a filamentous form, still with an overall randomly oriented molecular and lamellar texture. It is the drawing of these gel filaments, after or concurrent with solvent removal, and achieved by either heating or solvent exchange, which yields the final fibres of ultra-high modulus and strength.

We may conclude both from the preparation of the gels and from the final mechanical properties that the gel spinning processes of Smith and Lemstra [27] and of Pennings and co-workers [28, 55–60], although using different solvents and extraction procedures, are essentially the same. Both involve producing a single-crystal gel and then removing the solvent and stretching. Both agree that it is the physical entanglements and not the crystals which limit the ultimate drawability.

Thus it seems that the act of disentangling the polymer by means of a solution step allows the very large deformation needed to align and extend the chains and to produce strong, stiff fibres. For commercial purposes a continuous process is required, and one or other of the gel spinning techniques would at present seem to be favoured. However, these are complex processes involving many stages, and for a fundamental understanding of the underlying molecular processes it may well be best to return to the better-characterized discontinuous processes of single-crystal mat drawing, and the formation of shish kebabs from very dilute solutions.

Appendix

Gel spinning techniques

In the main body of the text we aimed to describe the basic principles of making strong and stiff polyethylene fibres using gel spinning methods. To do this we have tried to keep to general principles in which we have drawn heavily both on our own experience, and have taken some selected examples from the works of Smith and Lemstra [27]. In doing so we also made references to processes originated by several other workers. We shall now enlarge upon these methods, including also some early examples of gel spinning that are now mainly of historic interest only. To keep matters brief but comprehensive this section will be largely factual and technical, with an occasional comment of our own where warranted by our own experience.

The earliest work dates from two 1962 patents, which refer to solution spinning of polyethylenes of molecular weight 25 000 to 200 000 at high concentrations. Sato and Hirai [61] added solvent to the melt to give concentrations between 40 and 80%, while Jurgeleit [62] used lower concentrations of 10 to 18%. Sato and Hirai simply extruded fibres and then drew these at 130° C. They found, using the highest molecular weight material available to them, that they could produce fibres with strength of ~ 1.2 GPa. Jurgeleit made fibres by spinning his solutions through an air gap of 2.5 cm into a water bath, and then extracted the solvent (usually paraffin oil) with a non-solvent before drawing the fibres. He also developed a process in which a cold suspension of the polymer powder is passed through a heated tube containing a "worm" stirrer to make the solution, which was then pumped through an orifice to make the fibres. Fibres could be drawn to draw ratios of ~ 9, and for a molecular weight of ~ 150 000 strengths of ~ 1.2 GPa were obtained.

To our knowledge the first reports which actually refer to the gel spinning of polyethylene came from Zwick [16, 63] who was primarily concerned with the fast production of polymer fibres from solutions or gels. In the case of polyethlene he used napthalene as a solvent. Although he successfully achieved fibre-production speeds of up to 800 m min^{-1} he did not produce strong fibres. The lack of strength was possibly due to the fact that the gel-spun fibres were not deliberately drawn after spinning, and also that the gel in this case may have been of another quite different origin, from liquid–liquid phase separation within the spun fibre. This was indeed suggested by Zwick [16, 63], who quoted the spinning of polyethylene in napthalene as an example of spinning where the solvent is a theta-solvent for the polymer, and the theta-temperature lies between the temperature of the spinneret and that of the surroundings into which the fibres are spun [16].

After a substantial lapse of time we arrive at the present developments in gel spinning dating from the publication by Smith *et al.* [26] on solution spinning and subsequent hot-drawing of polyethylene of $M_w \sim 1.5 \times 10^6$, to give fibres with strengths ~ 3 GPa (a subject we attempted to cover and evaluate in the main body of the review. Here the following additions will be made which have played a significant part in the technical developments, with corresponding potential for the future.

Pennings' development of the porous-fibre method [55–60] has been extensively referred to above. Here we give some specific details. First, that in fact two such methods have been announced in succession. The common feature is the production of a porous filament, obtained by solvent extraction, which is subsequently drawn. In the first case the porous fibre is made by dissolving the polymer (usually in paraffin oil, although other solvents have been investigated [13]), extruding, and quenching in air to form a gel fibre from which the solvent is then extracted with a non-solvent to give a porous fibre. After hot-drawing this acquires high strength and stiffness. Several points of technological importance should be made. The gel fibres themselves, if undrawn, melt at ~ 130° C, indicating a lamellar structure for the gel as indeed Smook and Pennings [57] suggest. In order to achieve homogeneous gels and to minimize the severity of extrudate distortion due to melt fracture, they chose to use a very long capillary with a small entrance angle. They found that with this system the maximum wind-up speed during the gel-spinning stage is limited, because the strength of the gel fibre falls as the wind-up speed is increased. This may be prevented by the addition of aluminium stearate which acts to reduce the adsorption of long molecules on to the capillary surface. Our own experience [73], that stearates prevent the build-up of entanglement–adsorption layers, tends to confirm that this particular effect (the increase in maximum wind-up rate on addition of stearate) is special to the long capillary used by Pennings *et al.* [13, 55–58] and is connected with problems associated with adsorption along the capillary walls; this may be analogous to the adsorption–entanglement layers encountered in the surface-growth process [30, 31].

The second technique for the preparation of fibres, reported by Smook and Pennings [59], is a suspension-spinning technique which combines dissolving the polymer and extruding the gel in one piece of equipment. In this case, the solvent consisting of 80% paraffin oil and 20% trichlorobenzene was mixed with the polymer powder at ~ 5.6 wt%, and aluminium stearate at ~ 1.25 wt% was added to keep the powder in suspension. This suspension was then pumped along a copper tube ~ 5 m long which was heated to ~ 190° C. The resulting extrudate formed a gel fibre which could be wound up ready for extraction with a non-solvent to form porous fibres.

Recently a more complex route has been described by Kavesh and Prevorsek [29]. This process is very similar to that of Smook and Pennings [57]: the polymer is dissolved in a non-volatile solvent at 5 to 15%, the solution is spun and cooled to form a gel fibre, and the solvent is then extracted using what Kavesh and Prevorsek [29] call a volatile "solvent". In fact they actually used non-solvents such as methylene chloride to replace the original solvent, and then the second "solvent" was removed to leave a "Xerogel" which was a fibre similar to that of Smook and Pennings [57] but of lower porosity. These Xerogel fibres were then stretched in a two-stage process, the second drawing being at a higher temperature than the first. The mechanical properties they report are again closely similar to those of both Smith and Lemstra [27, 51–59] and Smook and Pennings [55–60], but the thermal behaviour is claimed to be different in as far as the melting points reported are unusually high, at least 147° C and in some cases as high as 160° C. However, it is well documented that by constraining fibres, so as to prevent them from shrinking when heated, one raises the melting point (e.g. [23]), and it is general experience that this in fact occurs when fibres are encapsulated in the DSC sample holders in the course of the usual melting-point determination by DSC. In our opinion this could be the cause of the high melting points, which would thus be artificially elevated, leaving no grounds for believing that the fibres discussed are intrinsically different to a significant extent from any of the others [51–60].

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