

ON THE GEL-SPINNING
- On the Passage of Ten Years After the Discovery -

by

M. Iguchi and H. Kyotani,

**Research Institute for Polymers and Textiles,
1-1-4 Higashi, Tsukuba, Ibaraki Pref. 305, Japan**

1.Introduction

In early 1980, Prof. Pennings was showing a visitor around his laboratory in Groningen, in North Holland. There was a Couette apparatus equipped with an outlet on the side wall and a fine filament of ultra-high molecular weight polyethylene was being drawn out and wound up continuously on a bobbin driven slowly by a laboratory-motor. The Young's modulus and the strength were said to be as high as >100GPa and 4GPa, respectively. This was the first instance for the visitor to see the prototype high-strength fibre which had surprised the world a few years ago¹⁾. On the next day, the same visitor was introduced to Dr. Paul Smith in a laboratory at DSM Research, Geleen, 300km south. When the host picked up a piece of filament and pulled, it elongated magically without break till the span of his arms. Nearby was a simple solution spinning apparatus apparently build up with a set of work-shop made components. He told that the material was nothing but polyethylene of ultra high molecular weight but coagulated from a dilute solution and that the mechanical properties were almost equivalent to those of the Pennings' fibre, presenting a reprint of a paper²⁾ which had just been published in a journal.

The second scene was particularly impressive. The fact that such a flexible polymer could be drawn and oriented at such an ease and smoothness was never in the comprehension of scientists, and industrial approach to a high-performance fibres was only found with polymers of rigid backbones as shown in the development of Aramid fibres. The new process could develop into a new technology for making a new super-strong fibre, giving a prestigious status to the common polymer which had been only of use for commodity purpose!

During the last ten years, a number of works have been done in a sensational atmosphere from both scientific and technological interest and the "gel-spinning" has been brought up on the initial stage of industrial manufacture, marketed under the names of Dyneema® from DSM-Toyobo Co., and Spectra® from Allied Chemical Co. Similar fibre, Technilon® has been also launched from Mitsui Petrochemical Co. on what is called "wax-blend method". The gel-spinning has also stimulated the development of high-strength materials, viz., from other flexible polymers, such as polyoxymethylene and polyvinyl alcohols. The progress has been followed from time to time in many articles, some of which being listed up in the reference section³⁻¹¹⁾. This paper is rather intended to give an overview to the development of the technology, including its background and periphery, with reference to some contribution from the author and his colleagues.

2. General background

Before getting into the main subject, let us briefly look back the past of artificial fibre-making which has been a consistent endeavour of mankind. As far as record exists, the first man who proposed an idea was Robert Hook, who wrote in 1664 in 'Micrographia' that "artificial silk could be obtained from glutinous solutions as silk-worm wire-draws his clew". A Frenchman, Reaumur had also questioned in 1734, "Silk is only a liquid gum which has been dried, could we not make silk ourselves with gums and resins?" Almost two centuries after Hooke's suggestion, the first patent of artificial silk was granted to Audemars who drew fibres, by means of needle, from a solution of gun-powder, specially prepared from "mulberry twigs". The use of a jet or nozzle was devised by Swan in 1886 and refined around the turn of the century when the solution spinning method was established by Coutaulds Company for the mass-production of viscose-rayon. The method for improving mechanical properties of fibres by applying a tension in the course of coagulation was worked out in this age, when the concept of macromolecular was yet to be proposed and recognized.

The occurrence of "necking" on the stretching of thermoplastic polymers and the progress of subsequent drawing with a constant draw ratio ("natural draw ratio", usually <10) was first studied by Wallace Carothers and his assistant in 1930s, elucidating the remarkable increase in molecular orientation and mechanical properties. The "cold drawing" process has been useful until now for the melt-spinning of fibres and the manufacture of oriented films. Nevertheless, mechanical properties of fibres and films attained by this method were judged to be far below from the ideal, when theoretical estimation became possible with the better understanding of molecular structure. For polyethylene, such a high value as 340GPa, almost one hundred times bigger than those measured for real specimens, was proposed by Mizushima and Shimanouchi¹²⁾ in 1949. (The ideal value ranges between 240-340 in literature. See, e.g., citation in reference¹¹⁾.) The discovery of lamellar single crystals of polyethylene in 1957 had given a enormous impact to the study of morphology of crystalline polymers. It was ironical, however, that the pursuit of strong fibres was rather discouraged, ever since the chain-folding was admitted as a general crystallization habit of flexible polymers predominant over the classical idea of bundle-like crystallization.

Effort for giving better orientation to polymers was continued by some groups. As will be discussed below, the barrier of the natural draw ratio was broken in the mid-1970s by Ward and his group¹³⁾, attaining a such remarkable Young's modulus as 70GPa by the drawing of polyethylene carefully recrystallized from the melt. Earlier in 1969, that a "single-crystal mat", or a pile of folded-chain type single-crystals, had such a high drawability as >30 times was reported by Ishikawa *et al.*¹⁴⁾, suggesting the possibility of "super drawing".

3. Characteristics and the drawability of the "gel"

Needless to emphasize, the most outstanding feature of the new method is based on a finding that an abnormally high drawability is bestowed to polyethylene of such a high molecular weight as $M_w > 1,000,000$, when the polymer is processed from a dilute solution, either in the form of a fibre or a film, whilst solidification of the same polymer from the melt usually forms a very tough material. Such solvents as decalin, tetralin etc. are used at elevated temperatures and the preferable concentration is 1-3%.

The interpretation of Smith and Lemstra¹⁵⁻¹⁷⁾ was such that a certain amount of inter-molecular entanglements would exist even in a dilute solution to form a continuous network,

by virtue of the largeness of the molecular length, and the network structure would be conserved through the process of precipitation to form a "gel", whilst gelation occurs only in a limited condition¹⁸⁾ and fragile aggregates of dendritic particles were usually formed with polymers of ordinary molecular weight. The maximum draw ratio, $\lambda_{\max}$ has been related to the solution concentration, c which determines the statistical mean distance between entanglements or the density of junction points. Thus,

$$\lambda_{\max} \propto c^{-1/2} \quad (1)$$

From this aspect, a favourite title, "gel-spinning" is not correct and "sol-spinning" may be a better expression, whereas another term, "gel-drawing" may be appropriate to describe the subsequent process. Apart from such terminological argument, the concept of "gel" or network has gained strong supports. For instance, a reconfirming result has been obtained by a follow-up experiment by Matsuo *et al.*¹⁹⁾, and ca. 0.4% has been pointed out to be the critical concentration of forming a continuous network for the class of polymers. The condition was optimum for giving high draw ratio (>200) and a Young's modulus >200GPa was recorded by simple drawing method.

Experiment to examine the drawability of gels, as well as resultant mechanical properties, has been operated in a wide concentration range by the present author *et al.*^{20,21,11)} and the applicability of *Equation (1)*, reconfirmed. *Figure 1* shows the original plot of Smith and Lemstra¹⁵⁾ in which new data have been added. The preparation of concentrated solutions, free from "fish-eyes", was carried out with two new techniques developed in cooperation with Mitsui Petrochemical Co., one being "the gruel method"²²⁾, in which polymer powder was soaked with a small amount of cold solvent and then hot solvent was added, and the other, "the controlled-heating method"²³⁾ in which the heating rate was controlled to be sufficiently low in the swelling region, i.e., 95-110°C, when the suspension of the polymer was heated.

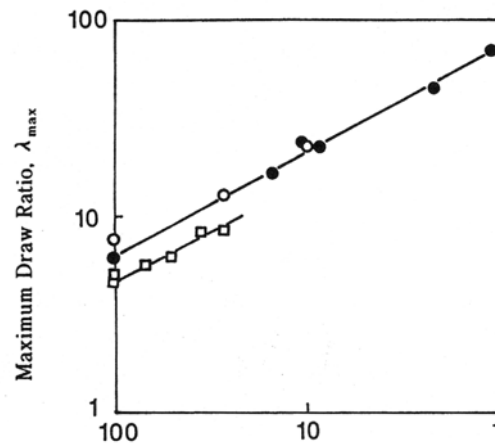


Figure 1 Maximum draw ratio of polyethylene gels, plotted versus original solution concentration.

- : Original data of Smith et al.(120°),
- : this work (120°C), □: this work (room temperature)

Thus, the network theory has been concluded to be sensible at least qualitatively. A question has remained, however, on what happens at molecular level in the actual drawing process of a

real specimen in which the entanglement-to-entanglement distance must have a wide distribution. Does not the destruction of networks, which presumably accompanies chain scission, become significant particularly in the later stage of drawing? It has been postulated, and examined to be factual, by Kyotani *et al.*²⁴⁻²⁶⁾ that a drawn fibre or film may consist of two parts; one part in which molecules have been well oriented but still constricted in the network structure, and the other, in which oriented molecules have been freed from the network with the breakage of linkage. A portion which has not been well stretched may be included in the second part.

In the DSC measurement of drawn films, it has been found that the endotherm around the melting split distinctively into two peaks, when specimens are placed in the sample-pan by fixing the length. *Figure 2*) shows scanning electron-micrographs of the surface of a drawn film before and after the sample was heated up to a temperature between the two DSC peaks by fixing the length, in which the track of discrete partial melting is observed clearly. The second DSC peak has been credited by Pennings and Zweinenberg²⁷⁾ to the hexagonal crystalline modification observed in the vicinity of melting by X-ray diffraction. It has been concluded that the whole of a specimen, which is exclusively orthorhombic at room temperature, melts all at once at a temperature, corresponding to the first DSC peak, and a certain part transforms into the hexagonal form under a tension. Then, the analysis of DSC peaks can give a measure for the evaluation of 'constricted' and 'free' parts assumed above. *Figure 3* shows the percentage transition, from the orthorhombic to the hexagonal form, determined for various drawn films. The appearance of a maximum in each curve is rendered to the consequence of the destruction of linkage or the scission of molecules. It is suspected that the amount of the 'free' fraction may be related to the mechanical performance of the fibre, viz., the relaxation property which has been pointed out to be a weak point of polyethylene fibres, although there has been no experimental evidence.

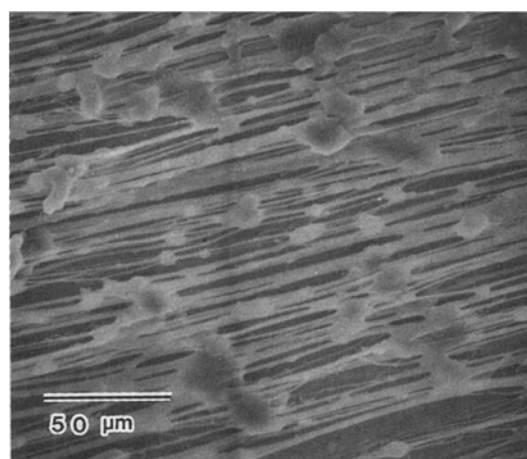


Figure 2 Scanning electron-micrographs of the surface of a drawn film after heated up to 120°C, which is between the two DSC peaks.

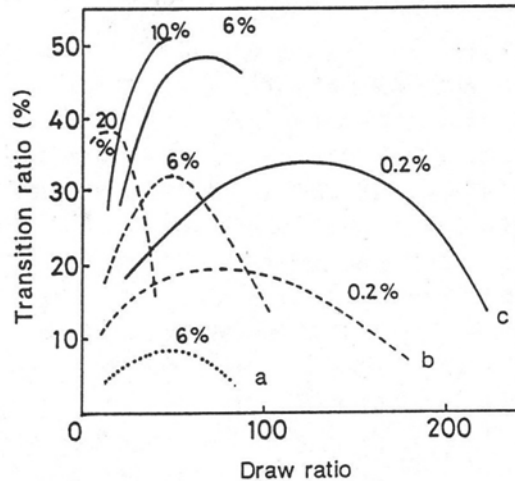


Figure 3 Percentage transition, from the orthorhombic to the hexagonal form, in drawn-gel films from various source polymers (plots are omitted). Figures denotes the original solution concentration.

A: Hizex Million 145, B: Hizex Million 240M, C: Hifax 1900

A computer simulation to verify the network theory has been carried out recently by Smith *et al.*²⁸⁾. Basing on a rather simple kinetic model which includes only the average molecular weight and solution concentration as parameters, not only the maximum draw ratio but also the stress-strain relationship have been demonstrated as Figure 4. It is quite interesting that the result has been obtained without taking account of such structural change as the 'unfolding' of molecules from lamellae, the destruction of spherulites, etc., which are widely believed to be important for the drawing of crystalline polymers.

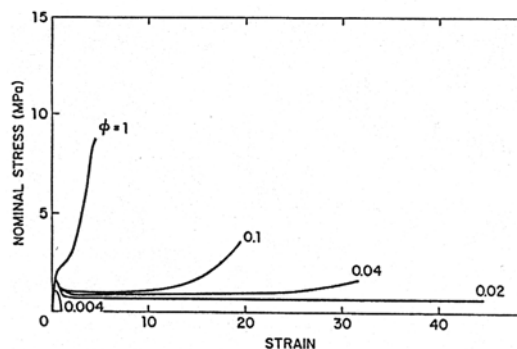


Figure 4 Stress-strain curves of polyethylene gel obtained by computer simulation by Smith *et al.*¹⁸⁾

ϕ stands for the solid fraction in solution.

4. Other Routes to High-strength Polyethylene Fibres

Besides the gel-spinning, several routes have been developed to obtain high-strength polyethylene fibres as summarized in the following.

(1) Drawing of melt-crystallized solid

The originality of the method developed by Ward and his group¹³⁾ was that cooling of molten polymer was conducted at an extremely slow rate for the preparation of precursor material, contrary to the traditional tactic for fibre-making in which quenching to low temperature was preferred. Then, super-drawing was successfully done at an elevated temperature some degrees below the melting temperature. It is considered that the slow progress of the crystallization would have given molecules good chances to slip out of the molten phase, giving rise to a structure with a low entanglement density.

The method is suitable for polyethylene of moderate molecular weight, not like in the case of gel-drawing, and the Young's modulus and the strength attained by this method were at the level of 70GPa and 1.7GPa, respectively. The industrial application of this method has been studied intensively, although products are yet to be found in the market.

(2) Drawing of "single-crystal mats" and other aggregates

"Single-crystal mat" originally studied by Ishikawa *et al.*¹⁴⁾ was a pile of lamellar type single-crystals grown in a dilute solution of polyethylene, of ordinary molecular weight. Drawability of >30 times was demonstrated and the change in molecular orientation was investigated in details. That good mechanical properties developed by this method was confirmed later by Furuhashi *et al.*²⁹⁾ with ultra-high molecular polyethylene. "Co-extrusion" of single-crystal mats, in which a specimen is sandwiched between polyethylene sheets, has been studied by Kanamoto *et al.*³⁰⁾ and a Young's modulus as high as 210GPa has been attained.

"Gel-press method" developed by Toyobo Co.³¹⁾ uses a semi-dilute solution and the precipitated "gel" is pressed into the form of a sheet, before processed through a dice, and such a high drawability as 150-200 is pertained. This method is said to be advantageous for making a thick diameter filament and a strong 'wire' (1mm ϕ , Young's modulus>150GPa, strength >2GPa) has been obtained.

That the entanglement in nascent polyethylene can be controlled by the selection of polymerization condition was found by Smith *et al.*³²⁾. A film was obtained on a glass plate coated with a catalyst had a high drawability and gave a strip having 125GPa Young's modulus.

(3) Melt-spinning with additives

The method, usually called the "wax-blend method"³³⁾, has been developed by Mitsui Petrochemical Company as another process for manufacturing high-strength fibres as mentioned above. Technologically, the method may be categorized in melt-spinning but such additives as paraffin and its derivatives are employed in order to give fluidity to highly viscous polyethylene. Thus, fibre can be spun from an mixture containing 30-60% polyethylene directly from an extruder and partial molecular orientation is given in the hot stage. The orientation is completed and the additive is removed in the following drawing process. The action of additives has not been much argued but it is considered that they may behave as a solvent or a diluent for polyethylene in the processing temperature which is far above their melting temperature. The process is said to be applied not necessarily to ultra-high molecular polyethylene and is suitable for polymers whose molecular weight is at the level of a half million.

(4) Direct Spinning from Couette-type apparatus

The unique method developed by Pennings and his group and mentioned on the top of introduction, has been developed on the extension of his early study on the formation of

"shish-kebab" structure³⁴⁾ in a poiseule flow of a dilute solution of polyethylene carried out in 1965, when he worked in DSM Research. He believed in the existence of "shish" consisting of extended molecular chains in the core of over-grown "kebabs" of folded-chain lamellae, although it has received some challenge. On the halfway to the new method, he manifested the certainty by obtaining such a high Young's modulus ca. 30GPa for a fibre-rich specimen extracted from shish-kebabs³⁵⁾. Shish-kebab structure itself had been formerly reported independently by Mitushashi³⁶⁾ in 1963 but the work had stayed at the level of morphological interest.

The mechanism of the formation of filament proposed was that a bundle-like crystal-growth would take place and continue at the tip of filament, in contact with the surface of the rotor, as the method is often called "surface crystal-growth method". It may be questioned, however, whether such an unique crystal-growth is possible in a turbulent system and continue in harmony with the pulling out of filament. Alternatively, it is conceived that molecules might be drawn out of a gel-like layer formed on the rotor surface and oriented subsequently under the winding tension.

5. Conclusion

With various method to obtain high-strength polyethylene fibre, what is in common is the practice of high drawing. As discussed in Section 3, the density of molecular entanglement is the primary factor which determines the drawability of gels. This factor is considered to be important also in other methods and the decrease of entanglements is actually exercised, to a large or moderate extent, through dilution with solvent or by the control crystallization process. Probably, the state of network structure, whichever "solid" or "gel" or "sol", is not important. The maximum draw ratio which can be reasonably estimated for gels from dilute solution, however, cannot explain high draw ratios achieved in some other methods. The destruction of network or the scission of molecular chain, pointed out by Kyotani *et al.* and also included in the computer simulation of Smith *et al.*, is considered to be the second important factor, viz. when the density of entanglement is relatively high.

In August 1989, Prof. Smith was back from Santa Barbara, California to receive, on behalf of the inventors of the gel-spinning, a Gold Medal of The Royal Dutch Chemical Society at The Summer Congress held, at Maastricht, close to Geleen. The visitor who first saw him nine years ago was happened to be there and joined the celebration of the award.

Acknowledgement

The lucky visitor is identified to be the present author. He wish to thank Prof. Lemstra, now in Eindhoven University, for his suggestion and encouragement for writing this articles. Thanks are also due to his colleagues, namely Dr.(Mrs.) Kyotani, for their valuable advice and discussion.

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