Review Article

Some developments in poly(ethylene terephthalate) fibre production and structure-property relationships

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Poly(ethylene terephthalate) (PET) fibre occupies the top place amongst the man-made fibres in the world today. During the past few years, very significant developments have taken place in the technology of its production. The resulting products like partially-oriented yarns and spin-draw yarns are already well established, while the yarns spun at very high speeds and the micro-denier fibres are showing promise as fibres of the future. These developments have been accompanied by a parallel upsurge in the research and development efforts on PET and its products due to which a more clear understanding of its structure and the underlying fundamentals of structure-property relationships are becoming available. As a result, products to meet specific functional requirements can be designed with increasing confidence. The various developments that have taken place in these areas in the past few years cover a very wide canvas and, therefore, only a few selected developments related to some physical aspects of PET fibre production and structure-property relationships will be considered in this article, the emphasis being on fundamental principles as far as possible.

Keywords: Poly(ethylene terephthalate) fibre, Fibre production, Fibre properties, Structure-property relationships

1 Introduction

Poly(ethylene terephthalate) (PET) fibre is today the most widely used manufactured fibre, having overtaken polamide fibres\(^1\) in 1972. Its fifty years of existence have recently been reviewed in a commemorative book\(^2\). Though the factors which have contributed to its success are numerous, the nature of the molecule is without doubt of utmost importance\(^3\). This is because the basic repeat unit of PET confers on the resulting semi-crystalline, oriented fibre a number of desirable features. These include, amongst others, thermal transitions which occur at the right temperatures and are of the right magnitude, and a relatively slow rate of crystallization. As a result, fibres can be produced with a combination of properties which make them suitable for a wide spectrum of applications. The present article deals with some of these aspects, the focus being on developments in spinning processes, fibrous products, structure and properties and their inter-relationships. In addition, the fundamentals involved in the extrusion or spinning process are also briefly considered and reference is made to some emerging application areas. The section on structure-property correlations deals with such important industrial processes as heat-setting and dyeing and with many important properties, e.g. mechanical and thermal properties.

2 Fibre Spinning

A schematic sketch illustrating the principal features of the melt-spinning process is shown in Fig. 1 for a single filament. The die-swell effect is assumed to be small and, therefore, neglected. The molten polymer is extruded at a specific rate through the spinneret hole into a transversely directed quench air stream and the spin line solidifies at some distance from the spinneret, indicated in Fig. 1 as the freeze line. A spin finish is then applied (not shown in the figure) and the solidified filament is finally wound up at a speed significantly greater than the extrusion velocity so that the cross-sectional area is about 100-200 times smaller than the initial area close to the spinneret exit.
2.1 Fundamentals Involved in the Spinning Process

2.1.1 Spinnability of the Fluid

One of the essential requirements for a fibre-forming polymer is that in the fluid form, it must be capable of assuming large irreversible deformation when subjected to a uniaxial stress field. This characteristic is called spinnability and is a necessary but not the sole condition for fibre formation.

The maximum thread length of the fluid is believed to be a function of two mechanisms of breakage. The first is a cohesive and brittle fracture occurring when the tensile stress in a viscoelastic jet exceeds its tensile strength and the second possible process of breaking fluid threads is associated with surface tension. Polycondensates like PET are very stable at take-up velocities of up to 4000 m/min and melt draw-ratios of up to 1000. On the other hand, melt-spinning of high molecular weight polyolefins is associated with serious limitations due to cohesive instability as their relaxation time may reach one second. It is essential for the spinning process that no spinnability limit be exceeded. When too low a viscosity of spinning fluid is used (e.g. too high a melt temperature), capillary break-up into individual droplets occurs due to materials with too long a relaxation time. The cohesive mechanism appears and only slow spinning is possible.

2.1.2 Role of Spinning Parameters

The spinning parameters are of paramount importance as they determine the fibre-line processability and the final product quality. The orientation that develops in the spin-line as a result of the tensile deformation under stress, is a function of the relative rates of extensional flow on the one hand and the disorienting thermal relaxation phenomena on the other. These rates, in turn, are governed by the velocity and temperature variations along the spin-line. Since the relaxation time in the case of polyester melt is very small (may be as small as 0.0001 s), the rate of molecular straightening must be very high for orientation to prevail.

The results of a study on computer simulation of melt spinning of PET up to wind-up speeds of 3000 m/min provide some insight into the role of spinning variables like melt temperature, intrinsic viscosity, polymer throughput rate, spinneret capillary diameter and temperature of cooling air on freeze line distance, the stress at freeze, initial force and uptake force. Melt temperature followed by the intrinsic viscosity of the polymer turn out to be the most critical process parameters. It is noteworthy that both these parameters control the melt viscosity and it may, therefore, be concluded that polymer rheology plays a crucial role in controlling the properties of the spun filament. The role of polymer rheology will therefore be discussed in sub-section 2.1.3. It is imperative to monitor closely and accurately the melt characteristics, more so for a multifilament multiposition melt-spinning plant. These parameters become even more critical at higher speeds of spinning and demand greater attention in ensuring uniform melt properties. From the simulation studies, the other parameters could be ranked in order of decreasing importance as follows: uptake velocity, throughput rate, spinneret dimensions and cooling air temperature and its velocity.

One of the conclusions from the above analysis is that the cooling air conditions do not significantly affect the spinline force, which is a predominant factor affecting the structure of the as-spun fibre. However, from the processing point of view, quenching conditions are of paramount importance as far as the uniformity of the spun filament is concerned. This point becomes clear when the simulation work is extended to gain an insight into filament acceleration and cooling rate during the spinning process. This work shows that for a wind-up speed of 1000 m/min, the filament acceleration peaks to 50000 cm/s (ref. 2) after 0.25 second of leaving the spinneret while the cooling rate shows a peak value of 4500°C/s after 0.27 second of leaving the spinneret. The corresponding figures for wind-up speed of 3000 m/min are 450,000 cm/s (ref. 2) after 0.23 second and 12,000°C/s after 0.23 second. The acceleration and cooling rate peaks are seen to lie
close to one another for any particular set of spinning conditions. The closeness clearly brings out the inter-relationship of the two important physical phenomena of melt-spinning, viz. heat transfer and mass flow. It also indicates the possibility of controlling the deformation rate by adjusting the cooling conditions, and thereby making attempts to minimize filament breakages during spinning.

2.1.3 Melt Rheology
It was earlier seen that one of the most critical parameters in melt-spinning is the melt viscosity of the polymer. Viscosity shows a strong dependence on the molecular weight and its distribution. In industry, the molecular weight is most conveniently and quickly assessed by measuring the limiting solution viscosity of the polymer in a suitable solvent. But it is the melt viscosity of the polymer which determines its flow behaviour and is of greater practical importance. However, in addition to molecular weight, the melt rheology is also dependent on the shear rate. Therefore, it is useful to relate the solution viscosity (intrinsic viscosity) of the polymer to its melt viscosity. A number of empirical relationships of the following type have been proposed for PET:

\[ \eta_0 = K (\eta^*)^p, \]

where \( \eta_0 \) is the melt viscosity at zero shear rate; \( K \) and \( p \), the constants; and \( \eta^* \), the intrinsic viscosity of the polymer. The following equation for zero shear melt viscosity (\( \eta_0 \)) was found:

\[ \eta_0 = (\eta^*)^{3.145} \exp \left[ \frac{8286}{t+273} - 4.6434 - 0.159 \text{ (DEG)} \right] \]

where \( t \) is the temperature of the melt in °C and DEG, the weight percentage of diethylene glycol in PET. The analysis also shows that PET melt flowing through a capillary is Newtonian close to the capillary axis and pseudo-plastic close to the wall of the capillary.

2.1.4 Filament Uniformity
The non-uniformity of linear density or diameter of the filament along the spinline has been shown in the literature to arise from a number of factors, some of which are internal (char, gel, pigment agglomerates, catalyst or stabilizer residues) or external (fibre waste and other substances) contamination, local variation in temperature or molecular weight leading to variation in polymer viscosity, instability of flow within the spinneret channels, non-uniform dimensions of the channels, temporary superheating of the spinneret which leads to formation of drips at low extension velocity, variation of extrusion velocity, temperature, take-up velocity, ambient temperature, equipment vibration, yarn slippage, etc. Studies on filament non-uniformity in PET have revealed that the presence of low molecular weight tail in the molecular weight distribution curve might be responsible for the thick and thin places in the filament, thus stressing the importance of a proper molecular weight distribution of the polymer used for spinning.

2.2 Developments in Melt-Spinning
Melt-spinning of polymeric fibres has witnessed a step change with the winding speeds increasing by an order of magnitude. The demand for high quality of the melts fed to the spinnerettes increases at high speeds. This increased quality requirement applies not only to polymer feed with respect to viscosity, homogeneity, freedom from dust, etc. but also to the processing conditions, involving proper drying and optimum melting conditions in the extruder. The propulsion and distribution of the melt to the individual spinning positions, including mixing and filtering, require more attention. To deliver a perfectly homogeneous melt, static mixers for distributive mixing are installed between the extruder and the metering pumps. The mixing elements consist of a lattice made up of cross-wise interlocking webs which are at an oblique angle to the pipe axis and are incorporated in the pipework of the spinning system. Quenching of the filaments needs special attention. Between 1937 and 1940, the first melt-spun polymeric fibre, viz. nylon 66, was extruded through spinneret holes at 285°C and cooled by natural convection down to 40-80°C before reaching the first contact points (finish application rolls, godets, etc.). A distance of 5-6 m at take-up speeds of 600-800 m/min was necessary for satisfactory cooling, corresponding to a cooling time of 0.7 second. The air boundary layer formed by the air friction on the filament caused poor heat convection and a certain instability in the thread path. A DuPont patent in 1939 stated that the boundary layer can be made as small as possible by cross flowing air, reducing the thread cooling path to 1.5 m, corresponding to a cooling time of 0.5 second. Many important developments in later years like inflow and outflow quench systems have reduced the cooling time to 0.05 second for fine yarns.

Control of thread tension in the wind-up zone becomes more difficult with increasing spinning speed. In contrast to conventional spinning, wind-up in high-speed spinning is carried out almost
exclusively without godets. In the 1000-2000 m/min range, the spinning dynamics is considerably affected by the rheological force while at higher take-up velocities, the dominant role is played by air drag force.

In high-speed spinning, the orienting influence of the uniaxial stress field overcomes to a significant extent the disorienting influence of thermal relaxation process. During melt-spinning, the temperature at which crystal formation commences is considerably enhanced at higher spinning speeds. However, molecular relaxation in the amorphous regions cannot be prevented. This has been a cause of disappointment to the fibre producers as oriented, crystalline fibres having the desired properties cannot be prepared by one-step process. Efforts are on to develop one-step technology (sub-section 2.3) as in addition to increased productivity, high-speed process also offers the benefit of reduction of energy and labour and reduction of total production cost besides, of course, being the simplest process.

The spinline crystallization of PET at high speeds involves significantly large undercooling; the melt temperature may decrease from 280°C to 180°C in 0.005 second. The nucleation rate is, therefore, very high and the concentration of nuclei is very dense. The crystal size of the nucleus for crystallization to proceed is considerably reduced and approaches the unit cell dimension of PET. This occurs because in an oriented melt, the entropy change on crystallization is small. At a given supercooling, the free energy change is correspondingly increased. This has been termed as nucleative collapse or as spinodal defect decomposition and is also referred to as regime III of crystallization. The large number of small nuclei come together to form a crystallite and the crystallization is distinctly different compared to the usual nucleation and growth process that dominates the crystallization of a melt in the stress-free state or at low stresses. For materials crystallizing fast and to a high degree (for example polypropylene), the increased crystallization rates at high spin stresses lead to well-oriented lamellar structures which form epitaxially on the originally fibrillar nuclei and fibrillar crystallites. For a slow crystallizer (such as PET), high spin-stress extrusion leads to an oriented, crystalline fibrillar system.

2.3 One-step Melt-spinning Technology

A one-step process based on high-speed spinning is very attractive for fibre producers. Though a patent, claiming that PET fully-oriented yarn (FOY) can be obtained by a one-step process with no drawing if spinning speeds exceed 4750 m/min, was filed in the U.S. as early as 1952, commercially available high-speed winders working in the 6000 m/min range were disclosed only in 1978 after which considerable activity was noticed in this area. Though high-speed spinning at 6000 m/min yields an oriented, crystalline fibre, the end-product is not equivalent to the two-step commercial fibre. This is because the relaxation time for molecules in the amorphous regions is very small and in spite of the spinning being very rapid, they relax to a significant extent with the result that the amorphous orientation developed is low and the mechanical properties are not totally adequate. Another problem is the pronounced skin-core structure that develops at these high speeds and affects the mechanical properties adversely. Commercial success has already been obtained in designing “spinline heating spinning” (SHS technique), which makes use of a hot tube below the freezeline to induce the slight additional stretch so that the conventional drawing step can be omitted. Control of the threadline dynamics by placing a hydraulic thread bath, which increases the tensile stress below the freezeline, has also been reported as an alternate route.

2.4 Other Spinning Processes

The melt-spinning technology described in the earlier sections is the simplest and the most elegant available spinning technique and is quite adequate for producing filaments from fibre grade PET or from the still higher molecular weight tyre cord grade PET. However, melt viscosity rises in proportion to \( M_n^{0.4} \) and molecular weights higher than the tyre cord grade PET are therefore not readily amenable to melt spinning. Solution and/or gel spinning techniques are therefore resorted to. The crucial factor in this spinning technique is the concentration of the polymer in the solvent for on this depends the density of molecular entanglements which, in turn, controls the drawability of the filament. Improved drawability allows draw ratios of 10-15 to be obtained, giving rise to higher molecular orientation and more structural continuity along the draw direction, as a result of which fibres have improved mechanical properties.

Another well-established production technology is the spin-draw process in which the spinning and drawing operations are integrated in a single unit.

The other spinning techniques like liquid crystal spinning and dry-jet wet spinning are used to produce fibres from aromatic polyesters or copolymers and are outside the scope of this article.
2.5 Molecular Theories of Fluid Flow

Molecular theories of flow have of late undergone a sea change with the result that the basic concept of how molecules move in a fluid has itself been transformed.

Molecular theories of flow allow a better understanding of the relationship between molecular parameters and rheological properties. In concentrated polymer solutions and polymer melts, there is a strong interaction between the molecular chains. Starting with the classical work of Eyring and his colleagues in the early forties, which involved a molecular segment as the unit of flow, the molecular theory was refined by Rouse to take into account the coordinated movement of the molecular chain segments. The innovative idea of reptation, in which a molecular chain is confined within a tube defined by its neighbours and moves by wriggling along a tortuous path, was conceived by De Gennes and translated into a quantitative theory of polymer chain dynamics of Doi and Edwards. Finally, Curtiss and Bird developed a kinetic theory for polymer melts and were able to predict the correct dependence of the zero shear viscosity on molecular weight.

3 Fibre Products

3.1 Introduction

The pattern for fibre production in all industrial nations is changing rapidly, moving towards lower volume but much higher value-added products for industrial markets. This has become necessary because the commodity fibres, which are principally used as apparel and household textiles, are dominated by acute pressure on price margins. Against this backdrop, the developing countries are expanding their production capacities for commodity fibres.

For the purpose of the present discussion, it is convenient to divide the man-made fibres in terms of their mechanical properties into the following three categories:

(i) Standard textile fibres with average mechanical properties: For this class of fibres, Atlas and Mark have laid down the following mechanical property requirements: Tenacity, 3-5 g/den; elongation-to-break, 35%; modulus of elasticity, 30-60 g/den; and completely reversible elongation up to 5% strain.

(ii) Industrial fibres with intermediate mechanical properties: For this class of fibres, Atlas and Mark have laid down the following property requirements: Tenacity, 7-8 g/den; elongation-to-break, 8-15%; modulus of elasticity, 50-80 g/den; and a high degree of toughness.

(iii) High performance fibres with excellent mechanical properties: This class of fibres has a tenacity of 15-50 g/den, elongation-to-break of 0.5-5% and modulus of elasticity of 250-2500 g/den.

To the above three conventional categories of fibre types, we may add a fourth category which bridges the gap in the mechanical properties between categories (ii) and (iii). The presence of this gap in mechanical properties was recently highlighted by Hearle. The fourth category is as follows:

(iv) Intermediate performance fibres with superior mechanical properties: This class of fibres will have a tenacity of 8-20 g/den, elongation-to-break of 5-15% and modulus of elasticity of 80-250 g/den.

These four fibre categories will be considered in this section. However, before discussing them it would be appropriate to include a brief description of the nature of the PET molecule and its likely contributions to fibre properties. A part of the molecule is shown in Fig. 2. The aromatic ring in the main chain with its attached carbonyl groups confers rigidity to the structure. It has been pointed out by Daubeny et al. that in an oriented fibre which contains an aggregate of such molecules placed parallel to each other, the distances between atoms in neighbouring molecules are all normal van der Waals distances; there is, therefore, no structural evidence for any usually strong forces between the molecules. The high glass transition temperature and melting point of the fibre thus arise mainly from the rigidity of the backbone. A number of other properties, particularly the mechanical properties, derive from the optimum combination of chain rigidity conferred by the aromatic ring and the flexibility derived from the glycol residue. The choice of this repeat unit is thus indeed a tribute to the foresight of its inventors. When many molecules come together, depending on the thermo-mechanical history to which the sample is subjected, they may form amorphous or semi-crystalline structures which are random or with varying degrees of orientation. In an oriented fibre, the structure is fibrillar in which a single molecule gets trapped in several growing crystals (Fig. 3). The detailed architecture of a PET fibre is still not known with certainty.

PET fibres can be spun over a broad range of spinning speeds, viz.:

(i) Low spinning speed in the range of 500-1500 m/min: The product is called low-oriented yarn (LOY) and PET staple fibre
and industrial yarns are produced through this route.

(ii) Medium speed in the range of 1500-4000 m/min: The product is called partially-oriented yarn (POY) and provides a feedstock for draw-texturing or for drawn flat yarns.

(iii) High speed in the range of 4000-6000 m/min: The product is called highly-oriented yarn (HOY).

(iv) Very high speed in the range above 6000 m/min: The product is called fully-oriented yarn (FOY). No commercial processes currently operate in this speed range.

The present article will lay emphasis on developments in fibres produced at medium and higher speeds.

3.2 Standard Textile Fibres

Category (i), viz. standard textile fibres, forms a very large application sector for PET fibres. It needs to be emphasised at this stage that though the bulk of fibres belonging to this category are used for standard textile uses, a number of non-woven products and also a variety of industrial fabrics are produced from standard textile fibres with average mechanical properties.

For convenience of discussion, the fibre products in this category will be considered under the following four headings with the emphasis being on developments in:

- Partially-oriented yarn
- Fully-oriented yarn
- Speciality fibres, and
- Micro-denier filaments

3.2.1 Partially-oriented Yarn (POY)

The high-speed spinning process has been described in an earlier section and the POY production technology forms a part of this broad area.

There are significant differences in structure development during spinning between the slow-crystallizing systems like PET, fast-crystallizing systems like polyamides and very fast crystallizing
systems like polyolefins. In the case of PET, though an oriented, ordered mesophase appears at spinning speeds of 1000 m/min and above, it is generally agreed\(^\text{18}\) that up to speeds of 4000 m/min, as-spun PET fibre is predominantly amorphous and is thought to be in the form of an entangled molecular network with an entanglement density of around \(2.3 \times 10^26\) per metre cube means that there are about 20 monomer units between successive entanglements\(^\text{19}\). However, some authors believe that the structure may not be homogeneous as in addition to the rubber-like network, crystal nuclei\(^\text{20,21}\) or extended chain molecules\(^\text{22}\) may also be present. As-spun nylon-6 also does not crystallize on the spin-line at low spinning speeds though crystallization occurs on conditioning in the package due to moisture pick-up. At speeds greater than 3000 m/min, however, crystals are generated during the spinning process itself. Polyolefins are fast crystallizing and polypropylene POY shows significant crystallinity even at low speeds.

PET POY became a commercial reality in the early 1970's mainly because of the availability of commercial winders around that time and also because of the introduction of simultaneous draw texturing. The polymer yarn producers were quick to realize that POY overcomes both the shortcomings of LOY (low-oriented yarn), viz. the shelf-life problem and the difficulty of stringing up, mainly because of the increased orientation, which gives the fibre storage stability and which allows heat-induced crystallization to occur at a temperature 30°C lower than for LOY. A further advantage of high-speed spinning is the higher thread uniformity obtainable from the more stable threadline provided by the higher draw down force which means higher threadline tension and by the increased frictional drag of air\(^\text{8}\). Subsequently, draw-warping was developed as a way of making flat yarns.

One of the most remarkable advantages of high-speed spinning is the increase in throughput per spinneret. In the case of PET yarn of fixed final linear density it has been shown\(^\text{23,24}\) that the throughput does not increase in proportion to the spinning speed as a consequence of the growing molecular orientation in the spun yarn; a gain of about 22% is obtained in throughput in going from 1500 to 2500 m/min, but there is only another 8% gain on going from 2500 to 3500 m/min. This arises because filaments of superior molecular orientation need a reduced draw ratio in a subsequent drawing process. This means that the linear density of the undrawn filament must be lowered provided the linear density of the drawn yarn is to be maintained constant. The following equation defines this relationship:\(^\text{23}\):

\[
M = (19000)\times DR\times WUS\times den
\]

where \(M\) = Mass throughput rate in g/min
\(\text{DR} = \text{Effective draw ratio}\)
\(\text{WUS} = \text{Wind-up speed in m/min, and}\)
\(\text{den} = \text{Denier of drawn filament}\).

The degree of molecular orientation and the productivity increase can be modified by other factors. Lower polymer molecular weight, through lowering the viscosity, leads to lower orientation in the yarn; reducing the threadline cooling rate by using a shroud or a secondary source of heat has the same effect; and higher filament linear density gives slower cooling and so operates in the same direction. Such modifications, therefore, lead to increased throughput at a given wind-up speed.

3.2.2 Fully-oriented Yarn (FOY)

Fully-oriented yarns can be obtained through different routes, the principal routes being as follows:

The POY route: POY has become universally accepted as a feedstock for textured yarn where further drawing and texturing get integrated in one process. Alternately, POY can be further drawn with the help of a draw twister into a fully-oriented flat yarn. Still another possibility is the use of the draw-warping method to achieve an FOY.

High-speed spinning route: This route has already been briefly referred to earlier. Though the yarn spun at 6000 m/min or higher speed is quite close to a FOY, it still needs a draw of around 20% to be equivalent to a two-step, commercial fibre. The spun fibre itself is used for a limited number of applications. Speeds higher than 6000 m/min are not very helpful as a relatively thick skin develops around the core of the filament and introduces a level of inhomogeneity that is not acceptable. Thus, one-step PET yarns have yet to become a commercial success.

Hot tube method: The use of a hot tube below the freeze line may allow a further draw to occur and a FOY of good quality can be produced using this method.

Spin-draw method: Integration of spinning followed by drawing in the same machine is now a well-established technique of fibre production.

3.2.3 Speciality Fibres

Speciality fibres include physically and chemi-
cally modified fibres, such as high-shrinkage fibres, modified dye variant fibres, profile fibres, hollow fibres, hybrid fibres, dyed fibres, textured yarns, bicomponents, high tenacity fibres, etc. The production volume of these fibres is presently very low in India and in view of their value addition role, it needs to be raised significantly.

3.2.4 Micro-denier Fibres

Strictly speaking, micro-denier fibres should have been discussed under sub section 3.2.3 but in view of their current importance, they are being taken up separately. It is believed that polyester microfibres may form up to 50% of the continuous filament market by 1995 and it is, therefore, not surprising that a very large number of publications are currently appearing on this product.

The first micro-denier was a PET fibre of 0.3 dpf (denier per filament) released by Toray in Japan in 1970. Teijin in Japan followed soon after and in 1972 released a PET and a polyamide fibre each of 0.15 dpf. In 1989, Toray released a PET fibre of 0.05 dpf, perhaps the finest microfibre in commercial use.

By using the conventional spinning methods and making use of specialized machines and good quality polymers, it is now possible to economically produce microfibres down to 0.2 dpf. Manufacture of fibres below this range is possible via various bicomponent splitting approaches down to 0.01 dpf; the splitting of the components being achieved either mechanically or through a solvent. A third method is based on dissolving one of the phases of a mixed melt-spun fibre containing two phases of an island-in-the-sea type. This gives ultra-fine fibres of about 0.001 or even lower denier.

The main advantages of microfibres can be illustrated by the following example. Compared to a PET yarn containing 1.5 dpf, an equivalent yarn containing 0.25 dpf will show:

- a reduction in flexural rigidity (which is proportional to the square of dpf) by a factor of 40,
- an increase in number of fibres per unit weight by a factor of over 6, and
- an increase in surface area per unit weight by a factor of 2.75.

As a result, there is a sharp change in fibre aesthetics. However, their production requires critical processing parameters. The spinning of PET microfibres through the conventional route has been reported by Kiang and Cuculo and the need for better filtration, proper static mixing and low spinline stress have been emphasized. In addition, these authors made the following points: A polymer of lower intrinsic viscosity of around 0.56 dI/g is better suited for microfibre production. When combined with higher temperature of extrusion, say between 295°C and 305°C, the elastic effects are reduced and low die-swell is observed. The lower viscosity allows the desired spinline stretch to be achieved at lower stresses. A lower capillary diameter ensures low draw down but it should not be too low otherwise shear rates become too high and die-swell increases. The authors have also described a number of other processing requirements for producing these fibres. They conclude that spinline stress is the most important parameter in determining the fine denier limit. The spinline stress is shown to be affected by the cooling profile, the elongational flow properties of the polymer as well as by the air drag generated in the spinline, which is the most important term determining the spinline stress level due to the very fast cooling of the fine denier fibres.

3.3 Industrial Fibres

Category (ii), viz. industrial fibres, also forms a very large application sector for PET fibres, particularly in industrially advanced countries like the USA where industrial polyester yarn consumption in 1991 was over 50% of the total polyester filament yarn consumption, with tyre cord alone accounting for 38%; the rest included seat belts, V belts, coated fabrics, cordage and other rubber goods like hoses. PET filaments have the advantage of a higher glass transition temperature and a much higher elastic modulus compared to filaments of nylon 66; these help in eliminating flat-spotting. However, the low strength and poor adhesion to rubber of PET filaments were two problems but they were soon overcome, the first by using PET of higher molecular weight of intrinsic viscosity 0.90 instead of the usual 0.61 dl/g. Multifilament yarn spun from this grade of polymer at a wind-up speed of 500 m/min could be drawn to a draw ratio of 6 to develop a tenacity of 8-10 g/den. The second problem, viz. that of adhesion, was solved by predipping the cord in a bath of an epoxide resin and a diamine before the rubber latex application. Today, the filaments are usually spun at a wind-up speed of 1500-3000 m/min and then drawn by a factor of about 2, the final tenacity and crystallinity being developed by heating and stretching during cord preparation.

Another growing use for PET industrial fibres is as a reinforcing fibre in hybrid composites of glass fibre and unsaturated polyester resin where
the PET fibres add to the impact and flexural strength of the composite. The geotextile area represents another large outlet for industrial PET fibres where its higher creep resistance is an advantage.

3.4 High Performance Fibres

The estimated value of crystal modulus for PET is 110 GPa while the highest measured value of modulus reported in the literature is 39 GPa for a solution-spun fibre from high molecular weight PET of intrinsic viscosity 2.6 dl/g drawn to a final draw ratio of 16.4 in three stages of draw, the final stage being at 200°C. Thus, in the present stage of development, PET can only provide a fibre in the lower range of mechanical properties expected of a high performance fibre. Fully aromatic polyesters or co-polyesters can give superior mechanical properties but they are outside the scope of this article.

3.5 Fibres Intermediate between Industrial and High Performance Fibres

The solution and/or gel spinning technique is capable of providing this category of fibres using solutions with a range of polymer concentration. However, fibres belonging to this category can also be produced through the simpler melt-spinning route using special drawing and annealing procedures.

The first such method makes use of the zone drawing and zone annealing techniques. An amorphous or very low crystalline as-spun fibre forms the starting material. It is drawn at a relatively low temperature to give a fibre of low crystallinity which is converted by zone annealing at a high tension into a highly oriented, highly crystalline fibre with little backfolding. A fibre with a modulus of 21.4 GPa has been produced by this technique. A second method uses two-stage drawing of a conventional melt-spun yarn, each stage being followed by an annealing step. This allows the molecules to lie close to each other over longer lengths in the crystalline phase and a modulus of 18.6 GPa has been obtained at a draw ratio of around 20.

4 Structure-Property Relations

4.1 Introduction

With the growing commercial success of PET fibres and the realization that its macroscopic properties are predominantly related to its fine structure, R&D efforts on structure-property relations have witnessed an upsurge all over the world. The fine structure of a fibre produced from a specific grade of a fibre-forming polymer is a function of a large number of processing parameters which can be grouped under three broad headings, viz. spinning, drawing and heat setting. By varying these parameters, a very wide variety of structures and morphologies becomes available, giving rise to a spectrum of properties.

The techniques used for characterizing fibres and fibre-forming polymers have also witnessed significant improvements and some new powerful techniques have also been added. In the earliest studies on fine structure of fibres, X-ray diffraction and electron microscopy made the major contributions. In the X-ray diffraction area, one of the important developments is the use of synchrotron radiation which has made it possible to make in situ studies of molecular rearrangements during mechanical deformation or heat-setting. The small-angle X-ray scattering has also benefited from synchrotron radiation whose brilliance is at least three orders of magnitude higher than that of radiation from a rotating anode, and which is produced as a highly collimated beam. In the area of electron microscopy, scanning electron microscope and the more recent scanning tunnelling microscope and atomic force microscope have made it possible to have more detailed structural and morphological information. The other techniques which are now providing significant amount of structural information are neutron scattering, fourier transform infrared and Raman spectroscopy.

4.2 Heat-setting and Its Effect on Structure

PET fibres and fabrics contain residual stresses whose magnitude is a function of the thermo-mechanical history to which the product had been earlier subjected. The presence of residual stress gives rise to thermal shrinkage which renders the product dimensionally unstable. Heat-setting stabilizes the structure of the fibre and the fabric by providing thermal energy to the molecules so that they take up positions close to equilibrium, thus relaxing the residual stresses. Fabrics may be heat set flat or pleated.

4.2.1 Crystallization on Heat-setting

PET is generally heat-set between 190°C and 225°C and the setting effects are associated with changes in crystalline morphology. Therefore, it is important to understand how crystallization occurs. There are three possibilities. The smaller, imperfect crystals can melt at the setting temperature followed by recrystallization into a new form. As opposed to this mechanism, solid state
transformation can take place in the following two ways. First, the molecules in the amorphous regions which are well-parallelized but not in register can, with the aid of thermal energy, gain enough mobility to reduce their free energy by forming small crystallites. Second, the larger existing crystallites can become more perfect by expelling the defects out of the crystal.

Crystallization is prohibitively slow below $T_g$ because of lack of molecular mobility and also above $T_m$ because of too much mobility. The rate of crystallization is maximum for PET around 180°C. PET is not a fast crystallizing polymer; the maximum crystallization rate for PET is stated to be 0.016/s while it is 0.14/s for nylon 6 and 1.66/s for nylon 66.

It is well known that polymers crystallize faster when they are oriented and it has been shown that the crystallization half time for PET reduces from 660 s for unoriented sample to 0.01 s for sample having a birefringence of 0.08.

### 4.2.2 Effect of Heat-setting on Structure

The effect of heat-setting on structure will be illustrated with some results obtained from extensive studies on commercial multifilament yarn (76/36/0), designated as control, which was produced from PET chips with a titanium dioxide content of 0.4% and a melting point of 258°C. Its average molecular weight ($M_n$) was 19,040. The polymer chips were spun at 290°C at a pressure of 1400 psi and quenched at 20°C in an atmosphere of 97% relative humidity. The take-up speed was 800 m/min and the average molecular weight ($M_n$) of the spun filament was 17,820. The spun multifilament yarn was stretched on a draw twister with a top godet temperature of 95°C and a plate temperature of 140°C. The winding speed was 642 m/min. The draw ratio was 3.92. The drawn yarn was heat set in a silicone oil bath at temperatures between 100°C and 250°C under two conditions, viz. when the yarn was held taut at constant length (taut-annealed or TA) and when the yarn was free to shrink (free-annealed or FA). The crystallinity, crystallite size and crystallite orientation factor are shown in Fig. 4(a) while the birefringence and amorphous orientation are shown in Fig. 4(b). The crystallinity and crystal size for both sets of samples increase with increasing heat-setting temperature. Crystallite orientation and birefringence (average orientation) register an increase with increasing heat-setting temperature for taut-annealed sample but decrease for free-annealed samples. The amorphous orientation factor decreases in both cases. The $T_g$ values of these samples, as determined by differential scanning calorimetry, are shown in Fig. 5 as a function of heat-setting temperature. It is noteworthy that at high temperatures of heat-setting, the $T_g$ decreases. The data are replotted as a

![Fig. 4(a)](image)

![Fig. 4(b)](image)
function of crystallinity in Fig. 6 and the highly crystalline samples are seen to have low $T_d$. This behaviour may be explained as follows. Up to heat-setting temperatures of $160^\circ C$, new crystals are formed by coming together of well-parallelized chains in the amorphous regions which increases the number of small crystals in the fibre. As a result, the fibre set at $160^\circ C$ contains a large number of small crystals so that the amorphous phase is highly constrained. Heat-setting at higher temperatures can result in the formation of crystals of larger size, sometimes by the fusion of smaller crystallites. The fibre consequently contains a small number of large crystals, thus reducing the constraints on the amorphous phase.

The low-angle X-ray diffraction studies on these samples revealed\(^6\) that in the as-drawn state, the PET multilament yarn did not have clear-cut boundaries between the crystalline and amorphous phases. Heat-setting of the yarn in the free-to-shrink condition introduces clear-cut separation between the phases and also results in increase in chain folding. Under constant length annealing the phases are not so distinctly separated and the folds are less, until the heat-setting temperatures are high.

4.3 Some Physical Characteristics of the Crystalline and Amorphous Phases

Some physical characteristics of PET fibre and its two phases are shown in Table 1. The higher density, melting point, modulus and orientation of the crystalline regions are noteworthy. Thus, if a semicrystalline polymer is considered as a two-phase system, it may be assumed that permeability in the crystalline phase is negligible compared to that in the amorphous phase as the crystalline phase with a relatively higher density is much more compact compared to the amorphous phase.

4.4 Stress-strain Behaviour
4.4.1 Yarns Spun at Different Speeds

The orientation that develops during the spinning process has a predominant effect on the mechanical properties of the as-spun yarns. This is evident from the true stress-strain curves of PET yarns plotted in Fig. 7 for various spinning speeds. The mechanical properties of the filaments spun at high speeds are quite different from those of conventionally drawn filaments. The yield stress rises and the natural draw ratio characteristic of low-oriented yarns first reduces and then disappears as the spinning speed increases.

4.4.2 Heat-set Multifilament Yarns

The samples used for this study were the same as described in sub-section 4.2.2, which had been prepared for structural studies, viz. the spun and drawn sample (called control) heat-set at temperatures between $100^\circ C$ and $250^\circ C$ in the free-to-shrink and constant length conditions. To illustrate the type of data obtained, the average stress-strain curves for the control and the free- and taut-annealed samples heat-set at $100$, $160$ and $220^\circ C$ for 1 min are shown in Fig. 8. It is noteworthy that the stress-strain curves for samples annealed at constant length are quite close to one another.
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Fig. 7—True stress-strain curves of PET yarns spun at different speeds shifted along the strain axis to match their natural draw ratios.

Fig. 8—Stress-strain curves for PET fibres heat-set for 1 min at 100, 160 and 220°C and for control sample (FA-Free-annealed, TA-Taut-annealed).

Another and to the control. The curves for the free-annealed samples, on the other hand, show considerable variation; in particular, they show a more distinct yield behaviour and their ductility increases with increase in heat-setting temperature. These differences in tensile properties arise from structural and morphological differences between these two fibre types which have essentially similar crystallinity. The main structural difference is that the orientation of the molecules in the amorphous regions is much lower in the free-annealed sample. The main morphological difference is that the two phases are more distinctly separated in free-annealed sample and they are predominantly connected in series. Both these factors lead to lower modulus, lower strength and higher extensibility of the free-annealed samples.

It is worth pointing out that the stress-strain characteristics of taut-annealed samples are closer to the regular PET filaments since most of the industrial heat-setting is under tension. A further interesting observation is that the stress-strain characteristics of the FA-160 yarn are close to those shown by a regular PET staple fibre.

4.4.3 Structural Changes During Tensile Elongation

The earlier data showed that there are considerable differences in the stress-strain behaviours of yarns which have been prepared by heat-setting the commercial drawn yarn at 220°C in the taut (TA 220) and free (FA 220) conditions. To gain an understanding of the structural changes occurring in these fibres during the tensile test, rheo-optical Fourier-transform infrared (FTIR) studies were made on PET films which were prepared from ‘Mylar’ PET film obtained from Du Pont. The film was semi-crystalline and was stretched in the Instron tensile tester at 140°C to a draw ratio of 2.5. The stretched film was heat-set in silicone oil at 220°C for 15 min in the taut and free conditions. Both samples were about 55% crystalline and their other structural charac-
teristics were also close to those of the TA-220 and FA-220 yarn samples. The samples were examined in the rapid-scan made on an FTIR and the following data were derived from the polarization spectra series acquired during elongation: (i) changes in the trans/gauche conformations of the ethylene glycol segments, (ii) the transient changes in crystalline and amorphous orientation, and (iii) chain unfolding.

In the FA sample, the orientation of the molecules in the amorphous phase showed a gradual improvement throughout the test, while chain unfolding occurred in the sample above 20% strain. This indicates that the predominant mechanism of deformation in this sample could be chain uncoiling in the amorphous phase followed by longitudinal slip processes within the sample. In the TA sample, chain unfolding occurred at low strains accompanied by slight improvement in amorphous and crystalline orientation. Thus, longitudinal slip appeared to be the main deformation mechanism in this sample.

4.5 Recovery Behaviour

Textile fibres are subjected to considerable strains during their life time and therefore to ensure dimensional stability, it is necessary to design fibres with good recovery characteristics. The stress-strain curves for PET fibres were shown to exhibit a pronounced yield region where the tensile modulus falls quite rapidly. At strains below the yield point, the behaviour is more nearly Hookean so that their elastic recovery on release of the stress is high. At strains above the yield region, viscous flow plays a larger part in the process of extension, and the recovery on release of stress becomes progressively poorer.

The elastic recovery and work recovery of PET fibres are excellent at strains up to about 5% in highly oriented fibres and up to 3% in relaxed fibres and in this range they are superior to those for nylon-6 fibres. At higher strains, they deteriorate sharply and become inferior to nylon-6. Typically, the immediate elastic recovery falls from about 98% at 1% extension to 65% at 5% extension. These values relate to instantaneous recovery at room temperature. At temperatures above \( T_p \), the measured recoveries can be poor.

There have been only a limited number of studies to gain an understanding of the structural features which influence recovery. The recovery behaviour of PET (2 GT) has been shown to be relatively poor compared to 3 GT and 4 GT fibres. This was attributed to the dominance of the amorphous phase in controlling recovery in 2 GT fibres while in 3 GT and 4 GT fibres, the crystallites also play an important role. Brody et al. analyzed the recovery data for a number of fibres including PET and concluded that recovery could be attributed to the elastomeric nature of the amorphous phase.

Some studies on PET yarns heat-set in the relaxed state and at constant length have shown that the samples heat-set at constant length have superior recovery behaviour. It has been suggested that at low strains the recovery behaviour is dominated by the amorphous phase in both the samples; since the taut-annealed samples have higher amorphous orientation, they show better recovery. At higher strains, in taut-annealed samples, both the crystalline and amorphous phases influence the recovery behaviour and this is mainly because of the parallel coupling between them. In the free-annealed samples, the amorphous phase dominates the recovery behaviour.

4.6 Dynamic Mechanical Properties

While the tensile stress-strain experiments provide information of considerable value, they provide little information on the lossy nature of the fibre. A convenient way of studying the transitions shown by PET is by making dynamic mechanical measurements. Typically, PET fibres show two transitions, one at about \(-40^\circ C\) which is called the \( \beta \)-transition and the other at about \( 110^\circ C \), the \( \alpha \)-transition or the glass transition. The \( \alpha \)-relaxation occurs in the temperature range \( 80-150^\circ C \) at a frequency of 1 Hz, the exact position being very dependent on structural factors such as crystallinity and orientation. For an unoriented and amorphous sample (low speed-spun PET), it is close to \( 80^\circ C \) (Ref. 44). When this sample is heat set, it develops crystallinity but is without orientation and the \( \alpha \)-transition is now seen to occur at about \( 110^\circ C \). If the as-spun fibre is drawn and then heat-set, the fibre is both crystalline and oriented and the \( T_g \) is seen at \( 130^\circ C \). The data for the commercial PET yarn before heat-setting (control) and after heat-setting at \( 220^\circ C \) in free condition (FA 220) and at constant length (TA 220) are shown in Fig. 9. The storage modulus is higher for the control sample and is quite close to that for the TA-220 sample. However, when heat-set in the relaxed state, the amorphous phase undergoes considerable disorientation and the storage modulus is not only lower but also shows considerable temperature dependence. The tan \( \delta \) values are also relatively high for this sample and are indicative of the faster rate of decrease of modulus in this sample. The loosely packed molecules in
the free-annealed sample account for considerable energy dissipation at $T_g$.

4.7 Dyeability Characteristics

Since standard, unmodified PET fibres normally contain neither basic nor strongly acidic groups, they are not generally dyeable with ionic or cationic dyestuffs. The most important class of dyestuff used for their colouration is that of disperse dyes.

Disperse dyestuffs are absorbed and retained through a process of solution in the less crystalline regions and are commonly applied as dispersion in water. Slight solubility in water is advantageous as it permits diffusion to the fibre surface but substantial solubility can lead to poor dye bath exhaustion. However, only a few disperse dyes produce even, moderate shades at the boil. Due to the high $T_g$ of PET, the diffusion rate is low and an adequate shade is not built up. There are various ways in which this problem has been overcome and has led to the development of carrier-free dyeable PET and cationic dyeable polyester. The latter is produced by incorporating an additive containing sulfonic acid groups in the PET chain during the polymerization process.

The earliest studies on dyeability of heat-set PET filaments with disperse dye were reported by Marvin who observed minimum in dye uptake at a heat-setting temperature of about 180°C. A similar minimum has also been observed for free-annealed and taut-annealed samples, as shown in Fig. 10 for 24 h dyeing at 130°C using C.I. Disperse Red 11. The higher dye uptake of slack-annealed sample is believed to be due to the availability of larger amount of free volume. The dye can either be sorbed into microvoids in the fibre following a Langmuir isotherm or can be molecularly dissolved into the free volume created by segmental motion.

The minimum in dye-uptake may be explained on the basis of fibre morphology as follows. At the lowest temperatures of heat-setting, new crystallites are formed in the control sample by coming together of parallel chain segments in the amorphous regions which increases the number of small crystallites. At 180°C, their number is very large and so the path through the amorphous regions is very tortuous. In the later stages of crystallization, the crystallites increase in size and the amorphous volume per crystal increases. The fibre has now a smaller number of large crystallites. The amorphous volume per crystal has been measured and shows a minimum at 180°C. It may be added that the decrease of segmental motion at 180°C due to the constraints imposed by a large number of small crystallites is also distinctly seen in the $T_g$ data presented earlier.

4.8 Optical Properties

A single crystal of PET will be characterized by three principal polarizabilities in the three principal directions. It will thus have three principal refractive indices and therefore two birefringences. Textile fibres are generally axially symmetric so
that the refractive indices perpendicular to the fibre axis are indistinguishable. The principal refractive indices for a fibre are therefore $n_\parallel$ for light polarized parallel to the fibre axis and $n_\perp$ for light polarized perpendicular to the fibre axis. PET filaments, whose draw ratio is generally around 4, have a birefringence $=(n_\parallel - n_\perp)$ of around 0.16 or above.

The birefringence is made up of three components, viz. orientational, distortional and form birefringence; the principal contribution coming from orientational birefringence.

The crystalline and amorphous phase contributions to orientational birefringence $\langle\Delta n\rangle$ are expressed as:

$$\Delta n = \langle \Delta n \rangle_{\text{cryst}} + \langle \Delta n \rangle_{\text{am}}$$

This equation can also be written as:

$$\Delta n = \beta \Delta n_{\text{co}} f_c + (1 - \beta) \Delta n_{\text{amo}} f_{am}$$

where $\beta$ is the degree of crystallinity; $f_c$ and $f_{am}$ the Hermans crystallite and amorphous orientation factors; and $\Delta n_{\text{co}}$ and $\Delta n_{\text{amo}}$, the intrinsic crystalline and amorphous birefringence respectively. The intrinsic birefringences of the crystalline and amorphous phases are for an ideal unit with all molecular chains well aligned. $\Delta n_{\text{co}}$ has been reported\(^{47}\) to be anywhere between 0.212 and 0.31. It was observed\(^{47}\) that the lower values arose from studies on cold-drawn fibres while the higher values were based on studies on heat-set fibres. It was suggested\(^{48}\) that if a perfect crystal had an intrinsic birefringence of $\Delta n_{\text{co}}$, then a crystal with perfection index $P_c$ will have birefringence $P_c \Delta n_{\text{co}}$, assuming that an ideally perfect crystal will have $P_c = 1$. The measured birefringence $\Delta n$ of a fibre of crystallinity $\beta$ and crystallite orientation $f_c$ can then be written as:

$$\Delta n = P_c \Delta n_{\text{co}} \beta f_c + P_{am} \Delta n_{\text{amo}} (1 - \beta) f_{am}$$

where $P_{am}$ is the perfection index of the amorphous phase; $\Delta n_{\text{amo}}$, its intrinsic birefringence; and $f_{am}$ its orientation. Since fibres have different degrees of defect density, the reported dependence of intrinsic birefringence on morphology is not surprising.

### 4.9 Thermal Characteristics

The thermal characteristics of PET include such important features as melting and crystallization and are of practical utility in heat-setting and shrinkage.

Melting represents the transition of a polymer from an ordered state to the disordered state of a liquid melt and in this sense is the opposite of crystallization which is a process of transition of a polymer from a disordered state to an ordered one. While low molecular bodies melt in a narrow temperature range, polymers melt over a very wide range of up to 100°C. The process of gradual decrease in the degree of polymer crystallinity as it is heated is known as partial melting and the temperature at which the last traces of crystallinity disappear is known as equilibrium melting temperature, $T_m^\text{eq}$.

At the melting point ($T_m$), equilibrium exists between the liquid and crystal phases and $T_m = \Delta H/\Delta S$, where $\Delta H$ and $\Delta S$ are the changes in enthalpy and entropy at melting. $\Delta H$ is related to the difference in secondary bonding strengths between the chains in the crystalline and liquid state, while $\Delta S$ represents the difference in order between the two states and is generally large for polymer chains which are flexible and hence capable of assuming a large number of conformations than stiff molecules.

If the PET fibre is constrained from shrinking in the DSC cell, $T_m$ can rise by 6-9°C and it is thus necessary to consider the effect of molecular orientation, both in the crystalline and amorphous regions, on melting point\(^{49}\).

The wide crystal size distribution in PET fibre and the presence of imperfections like chain ends in the crystallites result in the melting point not being sharp. In a fibre, crystallites form during cooling. In fibre production, as the fibre cools, crystallites form during spinning, the difference of temperature between the filament surface and the environment can be large and this can set temperature gradients of the order of 10,000°C/cm to 20,000°C/cm. This corresponds to temperature differences of 10-20°C between the surface and filament axis. The crystallites that are formed are therefore not of uniform size.

As far as crystallization is concerned, though fully extended chain has minimum free energy, the PET chains are known to crystallize by folding because in this way crystallization is most rapid. Thus, chain folding is due to kinetic reasons and the resulting crystals are not in their stablest state but will tend towards it whenever they have a chance, e.g. on subsequent heating. This explains why crystal size becomes larger on heat-setting. When a PET fibre is taken to a higher temperature during heat-setting, different mechanisms can become operative; one is the partial melting and recrystallization of the fold surfaces, the other results from a longitudinal translation of the polymer chains within the crystalline lattice, which becomes sufficiently softened to permit
such a transition. In addition to these two mechanisms, small regions of parallel molecules in the amorphous phase can also crystallize.

It has been observed that PET filaments, even when heat-set at 255°C in the relaxed state, retain substantial regions of parallel molecules in the amorphous phase can also crystallize. Particularly, in the early stages of heat treatment, the recoiling of the chains prevails over crystallization, causing positive shrinkage. Once crystallization begins, the rate of shrinkage decreases and is ultimately superseded by elongation. It has recently been shown that the speed of production of the fibres can play an important role in determining the interaction between shrinkage and crystallization.

The shrinkage of PET fibres is believed to arise from the tendency of the rubbery phase to coil up when subjected to temperatures above $T_g$ and also from the folding of molecules at higher temperatures. It has been reported that during isothermal heat-treatment of PET fibres, there is a competition between two processes: (i) recoiling of chains, and (ii) crystallization. In the early stages of heat treatment, the recoiling of the chains prevails over crystallization, causing positive shrinkage. Once crystallization begins, the rate of shrinkage decreases and is ultimately superseded by elongation. It has recently been shown that the speed of production of the fibres can play an important role in determining the interaction between shrinkage and crystallization.

References