X FIBER PROPERTIES

Properties of polymers are not as constant as properties of low molecular weight compounds. The large size of the molecules and the resulting state of not necessarily full thermodynamic equilibrium lead to a range of properties. Fibers are not an exception from such behavior.[1,2] Thus, polymer properties depend not only on the type of polymer, but also on the physical perturbations of the material during processing. For any given polymer one may define only a range of properties which may be obtained. The processing determines finally where within the range a property may fall. The physical changes taking place in processing may proceed in various ways, and depending on the specific perturbations, different types of properties may change in different directions and to relatively different degrees. A set of those physical perturbations a material undergoes during processing is commonly referred to as the material history. This character of *"one material with many possible properties"* makes polymers so interesting and valuable, despite that a certain degree of difficulty is involved in processing them.

This chapter summarizes the directions of changes various fiber properties may undergo depending on the changes in the polymer properties and on the changes of different "unit processes" in fiber formation. For general descriptions of fiber properties the reader is referred to the monographs in that field.

X.1 Properties Dependent on the Polymer

X.1.a Polymer Chain Structure

As stated above, the polymer determines the range of properties which may be imparted to fibers. The definition of the possibilities a polymer offers is for some properties known better than for others. Which of the properties are better defined in terms of processing seems to depend on the importance of the property; those of primary importance were researched first, knowledge of others may still lag behind.

Modulus of elasticity is usually considered as one of the more important properties, therefore it seems to be better described. The limits of modulus for polymer, and fibers, have been quite well established theoretically from calculations based on the deformation of polymer chains,[3-7] and from the velocity of propagation of deformation impulses.[8] Experimentally, the moduli were determined from the relationship between stress and the deformation of crystalline lattice as detected by x-ray diffraction.[9-12] The values of calculated and experimental moduli of elasticity for polymer crystals of fiber forming polymers are collected in table X.1. Figure X.1 shows the stress - strain relationships for the single chains of different kinds of polymers, but these relationships do not coincide with the stress - strain curves characteristic for fibers. The moduli of elasticity determined in the direction perpendicular to the polymer chains axis amount only to some 0.8 to 5.5 per cent of the modulus determined parallel to the chain axis. On the other hand, he moduli of amorphous polymers have been estimated to range only between $0.29 \cdot 10^{10}$ and $2.45 \cdot 10^{10}$ *Pa*. The maximum value represents cellulose,[8,9,15] though this is without consideration of the high performance polymers.[87,88] The anisotropy of modulus is very large indeed. And so is the disparity between the crystalline and amorphous properties.

Table X.1
Moduli of Elasticity of Polymer Crystals.

Polymer	Modulus of elasticity, $Pa \times 10^{-10}$			
	Parallel to polymer chain axis			Normal to chain axis
	Calculated		Experimental	
	from chain deformation	from impulse propagation[8,14]	from x-ray diffraction	
Nylon 66	15.7[4]	21	13.7[9]	
Poly(ethylene terephthalate)	18.2[7]		7.45[10]	
Poly(ethylene terephthalate)	14.6[4]	21.6	13.7[9]	
Poly(ethylene)	34.0[5]	19.4	23.5[10]	0.196[13]
syn-Poly(vinyl chloride)	16 to 20[6]	12.45		
Poly(isobutylene)	7.0 to 8.0[6]			
iso-Poly (propylene)	4.9[6]	8.74	4.11[10]	0.226[13]
Poly(vinyl alcohol)		16.8	24.5[10]	0.706[13]
Poly(vinylidene chloride)	9.8[8]	9.35	4.07[10]	
Cellulose	18.0[4]	13.8		
Cellulose	7.75 to 12.1[3]			
Cellulose	5.7 [14]			
Cellulose triacetate	5.89 to 8.83[8]	8.24		
Poly(acrylonitrile)	14.7[8]	13.25		

The moduli of elasticity of conventional fibers normally amount to some 3.75 to 22 per cent of the X-ray determined modulus of any given polymer. This is an obvious reflection of the dual nature of fiber structure, the crystalline - noncrystalline relations, both quantitatively and qualitatively. Qualitatively means, of course, the morphology. In high performance fibers the moduli may reach up to about 30 per cent of the X-ray determined moduli of a crystal of the respective polymer. The moduli fibers from the same polymer may span from 2 to 20 times higher than the moduli estimated for the amorphous segment of the fiber structure.[15]

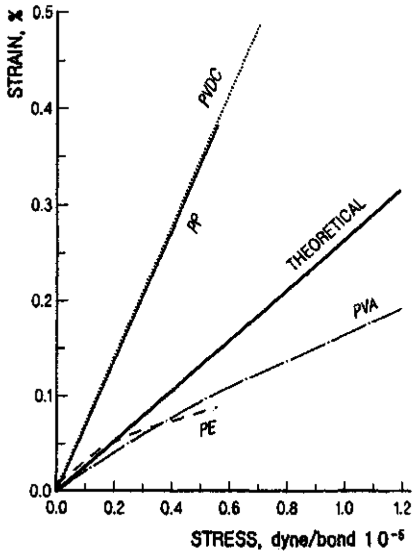

Figure X.1: *Stress - strain relationship for polymer molecules: the flat zigzag chain is indicated by the line named "theoretical"; poly(vinylidene chloride) (PVDC); polypropylene (PP); poly(vinyl alcohol) (PVA); polyethylene (PE). After Perepyol'kin*[8]

Investigations of the elasticity of polymer chains conducted by Sakurada and Kaji[12] indicate that the modulus of elasticity depends primarily on the chain conformation. Data supporting this conclusion are quoted in Table X.2 which gives the relationships of the mechanical chain properties in relation to the chain conformation. Figures X.2 and X.3 provide a communication reference regarding chain conformations. Those polymers which have fully extended chains, *trans*-configuration, have the largest force requirement for an extention of one per cent, which ranges from 4 to 5 *dyn/chain*. The force needed for extension of one per cent decreases with the extent to which the conformation deviates from that of a fully extended backbone. The force requirement reaches a minimum for the loose conformation of the type *trans' - trans' - gauche' - gauche'*. Conformations with regular helices have intermediate force requirement.

As one may conclude from the work of Sakurada and Kaji,[12] the modulus determined for amorphous polymers represents moduli based on the uncoiling of the amorphous molecules and not on the chain stretching. This is compatible with the views expressed in chapter V; the data reported by Sakurada and Kaji are for only one per cent of strain. At larger strains the situation may certainly look differently.

Sakurada and Kaji[12] report also another important observation: the level of forces acting in the direction normal to the chain axis, like in highly polar polymers,

Table X.2

Chain Conformations and Moduli[12]

Polymer	Chain conformation	Modulus of Elasticity $Pa \cdot 10^{10}$	Chain cross section area $m^2 \cdot 10^{20}$	Force for 1% chain strain *dyn*
Polyethylene	T (*zigzag*)	23.5	18.2	4.28
iso-Poly(propylene)	TG (3/1 helix)	3.4	34.4	1.18
Poly(vinyl alcohol)	T (*zigzag*)	25.0	21.6	5.4
Poly(vinylidene chloride), α form	TG'TG'	4.1	35.1	1.43
Poly(pivalolactone), α form	T'T'G'G' (2/1 helix)	0.65*	44.8	029
Poly(ethylene oxybenzoate), α form	—	0.59	49.8	0.29
Poly(ethylene terephthalate)	TT' (near *zigzag*)	10.1	20.4	2.24
Nylon 6	TT'T'TT'T' (near *zigzag*)	16.5	18.0	2.97
Nylon 66	TT'T'TT'T' (near *zigzag*)	17.3	17.9	3.1
Nylon 610	TT'T'TT'T' (near *zigzag*)	19.6	18.0	3.52

does not have an influence on the modulus in the direction parallel to the chain axis.

There were many attempts to relate the fiber moduli to the degree of crystallinity present in the fiber.[15,18] Those considerations were based on different models of distribution of the crystalline and amorphous areas. Successes of these efforts were limited; the obtained results better fit experimental data for bulk, unoriented materials rather than oriented fibers or films.

The *high performance* polymers, like poly(p- phenylene phthalamid) (*Kevlar*^{R}), poly(p–phenylene-benzo-bis-oxazole), poly(aryl- ether-ether-ketone), and others have very high moduli as one of the main properties qualifying them for the *high performance* group. What they have in common is the high degree of chain rigidity which results primarily from the chains built of cyclic monomers. Because of the high chain rigidity, even in solution the molecules do not coil but assume rod-like conformation. Consequently, these polymers crystallize predominantly in the extended chain conformation. Lack of the folded type crystallization leads to structures which are closer to the extended chain crystals rather than to conventional fibers. The noncrystalline fraction present in those polymers is mostly due to imperfections in polymer chain structure or due to some steric hindrances during crystallization process. In general, crystallinity of such polymers is very high. Quite naturally, the structure - property relationship for such polymers deviates significantly from that for the polymers with flexible chains. For example, the rigid chain polymers show modulus in the direction parallel to the chain axis comparable to steel or glass.[19] Some of the commercial fibers have moduli exceeding 1000 g/den, while theoretically it is possible to reach around 2500 g/den.[20]

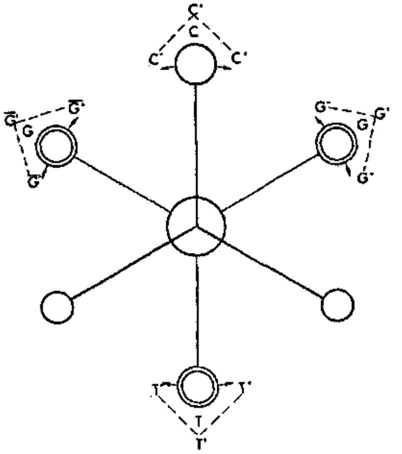

Figure X.2: *Diagram of various chain configurations: C for cis, G for gauche, T for trans. The superscripts indicate a deviation: positive, negative, or general (apostrophe). After Sakurada and Kaji*[12]

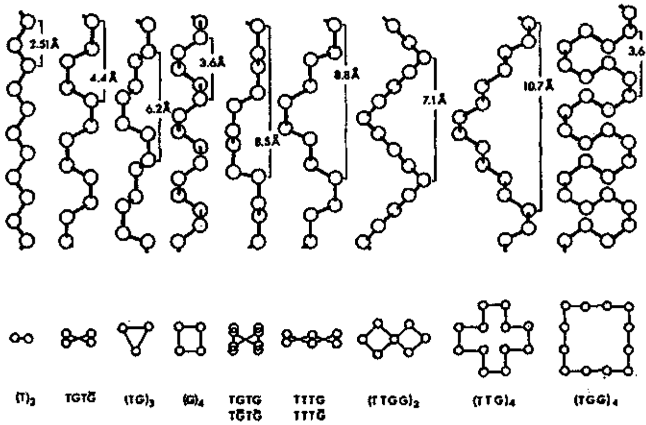

Figure X.3: *Basic chain conformations for linear polymers. After Bunn*[16] *and Mizushima et. al.*[17]

Another group of high performance fibers may be obtained from polymers with flexible chains *via* very extensive drawing (ultradrawing). The spun fibers which perform best in ultradrawing are made from polymers with a low level of chain entanglements, *e. g.* in gel spinning. The drawing is performed in several stages, so to assure chain propagation within the crystal. Ultimately, this leads to fiber structures approaching straight chain conformations. Similar results are obtained with solid state extrusion.[91&ref]

The basic properties of polymers, as usually quoted in the literature, may be greatly affected by irregularities in polymer structure or by impurities. Impurities are understood here as the fractions of polymer with molecules of greatly deformed structure or a larger amount of additives. Inclusion of abnormal monomer addition, as for example of syndiotactic - isotactic, or head-to-head nature, may strongly affect crystallinity and the crystallization process by affecting chain conformation, mostly by making the chains more flexible. Similar effects may result from low molecular mass impurities, but if not present in larger quantities, they may be somewhat less harmful as it is possible for them to undergo some kind of fractionation during the processing. During a crystallization process the low molecular mass impurities are usually pushed into the amorphous phase, though the crystallizability and crystallization kinetics will, most likely, be affected.

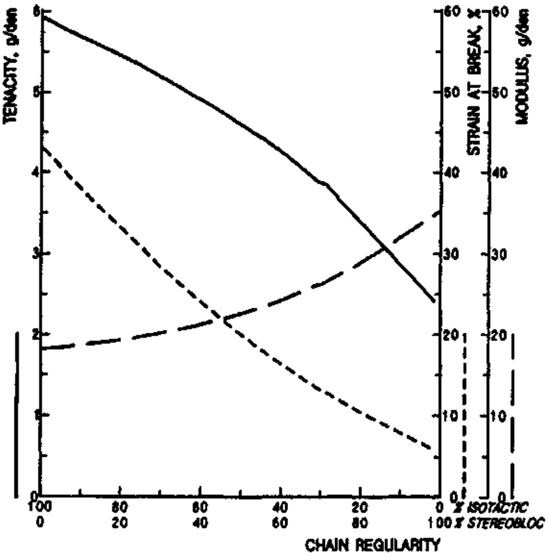

Figure X.4: *Tensile properties of polypropylene fibers in relation to the regularity of polymer structure. After G. Natta*[21]

Chain imperfections mostly can not be expelled or fractionated, and therefore may cause either a decrease of crystallizability, or a change of crystallization rate, or both. The influence of imperfect polymer structure is exemplified in figure X.4 where there are given tensile properties of polypropylene fibers in relation to the stereoregularity of polymer. The magnitude of the effect requires no additional comments.

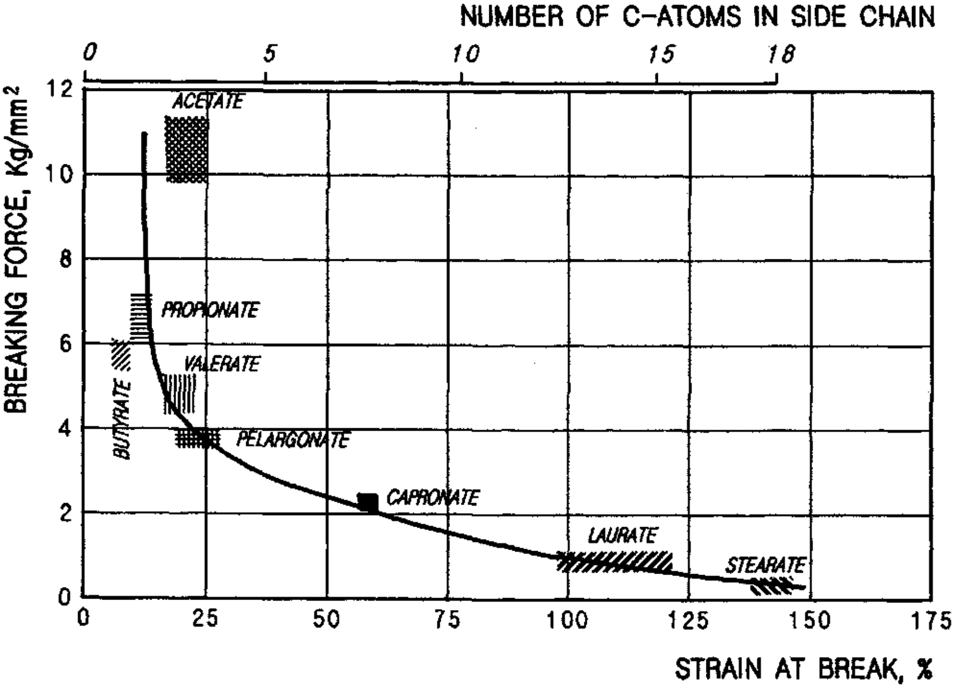

Figure X.5: *Tensile properties of fibers made from cellulose esters with different lengths of side chains. After Hagedorn and Möller.*[22]

Chain branching, an additional kind of structural irregularity, may have an effect similar to other chain imperfections; a decrease of crystallinity and crystal perfection are mainly observed. In general, short branches in large numbers are more detrimental than a few very long ones. The influence of the side chain length on fiber tensile properties is exemplified in figure X.5 which presents data for the series of cellulose esters of different length of the acid chain.[22] This is an excellent example showing the influence of the side groups with increasing uniform length. Full analogy should be expected between the cases of side chains resulting as a reaction byproduct and the effect of the side chain introduced on purpose; the effect on polymer properties must be expected to be equivalent. This principle is the basis for the development of the linear low density polyethylene (LLDP). The difference is that in the case of the abnormalities arising in synthesis, the side chains are usually of variable length so no such nice graph could be produced.

One must take seriously the possibility of cross linking of polymer chains. Often the fraction of cross linked polymer is encountered in small quantities, about 0.0001%. If the quantities are so small, they may have an influence on the resulting fiber modulus. However, processing of such polymers is proportionately more difficult. A gel content higher than some 0.0005% normally causes major problems with formation, primarily with the process continuity, with filament breaks. Filters become clogged easily, which also leads to process discontinuity. If the cross links are generated after the fiber formation, then this represents an entirely different, usually more positive situation.

X.1.b Effect of Molecular Mass

A strong influence of molecular mass on the mechanical properties of fibers was realized already in the very early days of fiber formation history, primarily in connection with cellulose fibers.[2] With progressing development, the originally proposed relationships were confirmed for other polymers.[23,24] H. F. Mark published the dependence of fiber tensile strength on molecular mass already in 1932.[25] Mark's relationship, although entirely general in nature, is shown in Figure X.6 for the case of nylon 66.[26] The relationship was presented in the following mathematical form.

$$\Theta = \Theta_\infty - \frac{B}{M_n} \tag{X.1}$$

where Θ is fiber tenacity originally expressed in the weight titer (denier), Θ_∞ is a constant equal to the fiber tenacity at infinite molecular mass, B s a constant depending on the polymer, and M_n is number average molecular mass.

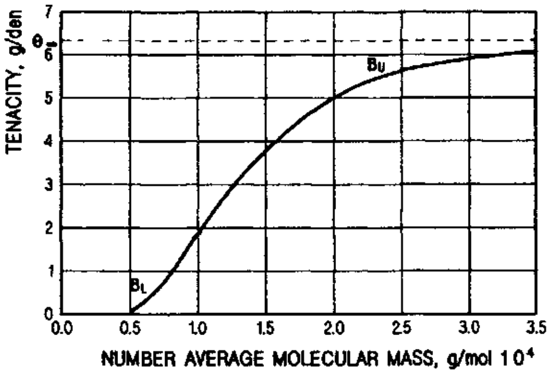

Figure X.6: *Dependence of fiber tenacity on number average molecular mass for nylon 66. After H. F. Mark*[26]

Mark's relationship was confirmed by Sookne and Harris[23] and elaborated on by P. J. Flory,[27] who found it more convenient to plot the data against the reciprocal number average molecular mass, or even better, the reciprocal degree of polymerization.

The curve reproduced in figure X.6 has two transition points indicated as B_U and B_L. If the molecular mass is smaller than that corresponding to B_L, no fiber with useful properties may be obtained. If the molecular mass is increased beyond the point B_U, no significant gains of tenacity is observed, the extra effort to produce and process higher molecular mass polymer is wasted. The part of the curve contained between the two transition points, B_L and B_U, is steep and, in industrial practice, operation on such a steep slope is not advisable, small variations in the molecular mass of a commercial polymer may cause large changes in fiber properties resulting in nonuniform product quality. Ideally the molecular mass of the polymer should be slightly higher than the upper transition point, B_U. For some polymers, mainly for those obtained in polycondensation reactions, use of high molecular mass polymer may be unfeasible due to the high costs of the appropriate polycondensation reaction. The transition points for different polymers are quoted after H. F. Mark in Table X.3.[26]

Table X.3

Transition Points in the Influence
of Molecular Mass on Fiber Tenacity.

Polymer	B_L Number average molecular mass g/mol	B_L Number average molecule length Å	B_U Number average molecular mass g/mol	B_U Number average molecule length Å
Nylon 66	6000	425	24000	1800
Nylon 6	6000	452	24000	1810
Poly(ethylene terephthalate)	8000	440	30000	1300
Poly(acrylonitrile)	15000	705	45000	2110
Poly(vinyl alcohol)	15000	870	45000	2600
Cellulose	20000	575	75000	2160
Poly(vinylidene chloride)	25000	515	75000	1920
Polystyrene	60000	1440	300000	7230

Although the molecular masses of the transition points vary substantially for polymers of different kind, the lengths of the stretched molecules are similar within relatively narrow limits. The data of table X.3 indicate that the strong polarity of a polymer tends to decrease the length of the molecule corresponding to the B_U transition. The trend is reverse for polymers with poor crystallizability. It is necessary to underline the apparent contradiction of this finding and the statement made in the previous section that the polar forces do not influence the polymer modulus. The only way the discrepancy may be explained is that here it concerns the fibers, their crystalline and amorphous phase, while in the previous section the questions were related to the crystalline phase only.

The relationship between tenacity and molecular mass was the object of many re-examinations by different authors. In cases when Mark's results were challenged, the experimental evidence invariably was in doubt.

The fact that the potential fiber strength depends on number average molecular mass has important practical implications. With the increasing broadness of molecular mass distribution and constant number average, the weight average, naturally, must increase. Since rheological properties are proportional to the weight, or to z- average, or to a combination of both, the increased breadth of the molecular mass spectrum requires more mechanical work without any gains in fiber strength. Since relaxation time changes in a way similar to the other rheological properties, widening of the molecular mass distribution must change the whole processing characteristics at potentially unchanged maximum of the obtainable fiber strength.

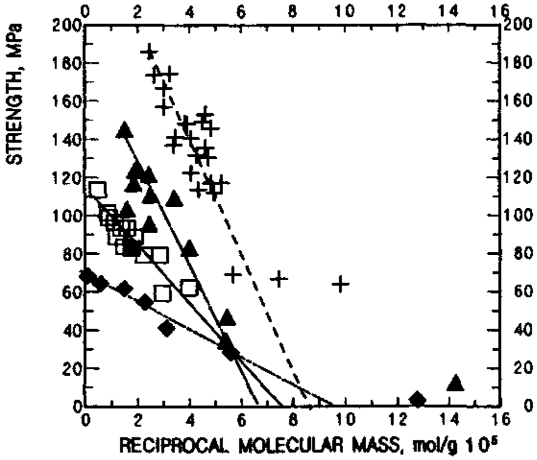

Figure X.7: *Strength versus reciprocal number average molecular mass. Open symbols denote monodisperse (fractionated) samples, filled points denote polydisperse samples, crosses denote bending strength at* $-196°C$. *Squares – cellulose acetate,*[23] *crosses – poly(ethylene),*[32] *triangles – aromatic polyimide,*[33] *diamonds – poly(methyl mathacrylate).*[36]

The strength of polymers depends also on the number of chain entanglements or *enchainments* present in the polymer.[6,28--30] Figure X.7 presents the relationships between the reciprocal number average molecular mass and the breaking strength for a number of polymers. The good correlation, considering the matter and the experimental problems involved, of the data is quite well visible. The values of M_t, it is of the molar mass where the polymer strength reaches zero, are close to the values of B_L quoted in table X.3. It has been suggested[31] that there is a relationship between M_t and molar mass critical for formation of entanglements $M_t = 2M_e$.

In brittle materials, the tensile strength is assumed to result from the simultaneous fracture of all the load bearing bonds in the cross section where the fracture takes place.

$$\Theta = n\ f \tag{X.2}$$

Here Θ is strength (tenacity), n is number of load bearing bonds per unit of cross section area, and f is the strength of an individual bond.

F. Bueche[34] proposed the following formula to calculate the maximum strength.

$$\Theta_\infty = n\ f = \left(\frac{\rho N}{3M_e}\right)^{2/3} f \qquad \text{at } M = \infty \tag{X.3}$$

The notation here is: Θ_∞ – maximum attainable strength, ρ – density of polymer, N – Avogadro's number, M_e – Molecular mass critical in respect to the entanglements.

To equation X.3 D. T. Turner[30] applied Flory's end correction factor[35] to obtain the following equation for strength.

$$\Theta = n\,f = \left(\frac{\rho N}{3M_e}\right)^{2/3} f\left(1 - \frac{2M_e}{M}\right) \tag{X.4}$$

Further, by combining equations X.3 and X.4, Turner obtained an equation very similar in form to the Mark-Flory equation X.1.

$$\Theta = \Theta_\infty - 6.8 \cdot 10^{15} \rho^{2/3} M_e^{1/3} f\left(\frac{1}{M}\right) \tag{X.5}$$

Thus, it appears that the number average molecular mass is really the determinant of of the obtainable fiber tenacity, however, there is still no certainty. Intuitively, one might expect that molecular mass distribution ought to play some, though not a necessarily large, role. More research is needed for full clarification of the issue. There seems to be no doubt, though, about the role of entanglements in the strength of polymers.

A role similar to the molecular entanglements are played by those *hard blocks* in the block copolymers which work on the basis of high glass transition temperature. A functionally similar role is played by those hard segments which are based on strong intermolecular forces, though there is some difference between the two.

X.1.c Thermal Properties

The equilibrium melting points are constant in polymers, but they rarely may be reached in practice. One may treat them as a theoretical limit. How much of this potential will be reached in any given fiber depends on the processing; melting point of crystals depends on the temperature of their growth.

Since normally polymers are not all crystalline, one needs also to take note of the amorphous material. Its basic properties, like chain flexibility and relaxation character (to a large extent, but not completely) belong to the material character. The whole rest, in terms of its behavior, depends on the processing.

Presence of a solvent causes differences in the polymer crystallization and melting, it also influences the behavior of the noncrystalline fractions, particularly in terms of accumulating stresses and in their relaxation. Presence and absence of solvent is a processing feature and as such is discussed in section X.2.b and in chapter VII.

X.2 Influence of Processing on Properties

The effects of *history* of the mechanical and thermal perturbations on polymers are discussed over large portions of this book. Mostly the discussion is of the *shear* *history* and, to a lesser degree, the *not so near history*. Technologically speaking, the *near*, and *not so near*, history is nothing else but the effects of a processing of the raw material, as well as sum of relaxation processes which took place at different stages. The term *history* in this case is a kind of "shorthand" convention to describe the influence of a processing on the fiber properties. Naturally, it is an indirect influence *via* the the influence on fiber structure.

X.2.a Tensile Properties

Cold drawing (or neck drawing) is the principal mean of building up the tensile properties of fibers. The potential effect of neck drawing depends on the structure of undrawn (or spun) fibers.[83,89] There are some authors[84--86] who claim the opposite, in disregard of what has been found over the years of fiber industry existence. The structure of undrawn fibers depends on the type of the formation process, as well as on the details of the process conditions, and the last relationship is of a high sensitivity. Naturally, as discussed in the preceeding section, everything takes place within a framework offered by the polymer in question. All of these truisms were realized for a long time,[37–39] though not described in easily accessible way.

An interesting opinion about the relationship between molecular mass and type of process has been expressed by the team of P. Smith, P. J. Lemstra, and J. P. L. Pijpers;[40] their opinion is represented in figure X.8.

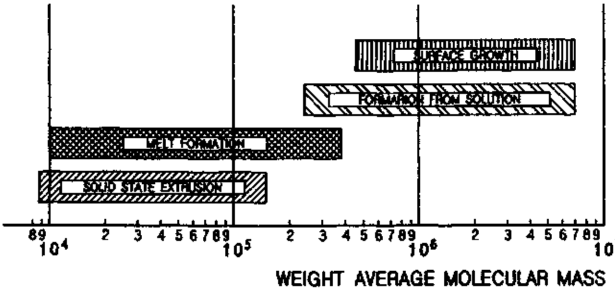

Figure X.8: *Approximate match between the type of process and molecular mass for polyethylene. After P. Smith, P. J. Lemstra, and J. P. L. Pijpers*[40]

The scheme of figure X.8 is somewhat idealized since, depending on the polymer and its chemistry, there are limitations on the attainable molecular mass or solubility. Nonetheless, the same authors published interesting data on the property buildup in fibers formed from polyethylene, depending on the molecular mass and on the type of process. Some of their results are presented in figures X.9 and X.10. The first of the figures presents the relationship between the initial modulus and tensile strength if a fiber formed from the melt is cold drawn to various degrees. The three different curves represent molecular masses: $M_n = 13 \cdot 10^3$ and $M_w = 100 \cdot 10^3$; $M_n = 28 \cdot 10^3$ and $M_w = 115 \cdot 10^3$; $M_n = 110 \cdot 10^3$ and $M_w = 120 \cdot 10^3$. Thus, the weight average molecular masses are close to each other and the number averages vary widely. Figure X.10 presents similar data but on fibers formed from a solution and cold drawn, as the previous set. The molecular masses were: $M_n = 120 \cdot 10^3$ and $M_w = 800 \cdot 10^3$; $M_n = 150 \cdot 10^3$ and $M_w = 1.1 \cdot 10^6$; $M_n = > 300 \cdot 10^3$ and $M_w = 4 \cdot 10^6$.

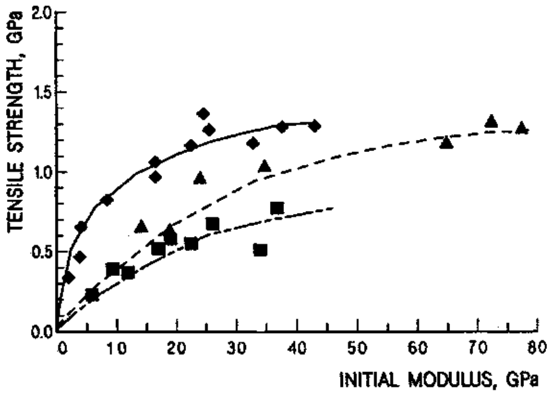

Figure X.9: *Tensile strength-modulus relationship for fibers formed from melt and neck drawn to various draw ratios. Squares* – $M_n = 13 \cdot 10^3$ *and* $M_w = 100 \cdot 10^3$; *triangles* – $M_n = 28 \cdot 10^3$ *and* $M_w = 115 \cdot 10^3$; *diamonds* – $M_n = 110 \cdot 10^3$ *and* $M_w = 120 \cdot 10^3$. *After P. Smith, P. J. Lemstra, and J. P. L. Pijpers*[40]

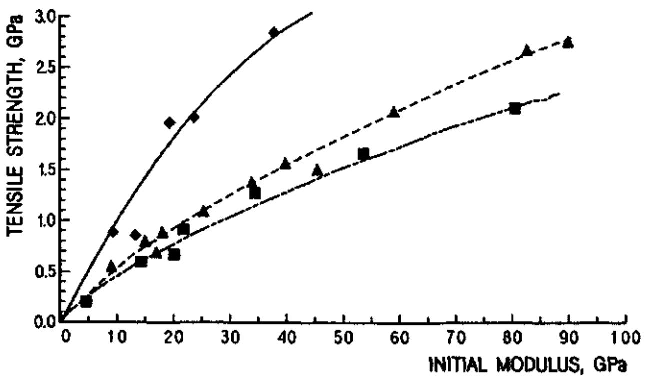

Figure X.10: *Tensile strength-modulus relationship for polyethylene fibers formed from a solution and neck drawn to various draw ratios. Squares* – $M_n = 120 \cdot 10^3$ *and* $M_w = 800 \cdot 10^3$; *triangles* – $M_n = 150 \cdot 10^3$ *and* $M_w = 1.1 \cdot 10^6$; *diamonds* – $M_n = > 300 \cdot 10^3$ *and* $M_w = 4 \cdot 10^6$. *After P. Smith, P. J. Lemstra, and J. P. L. Pijpers*[40]

In both of these figures, the maximum obtainable tenacities appear to fit the equation X.1, with the data scatter not larger than any other sets. What is important here is the good depiction of matching the method of formation with molecular mass. The second point is that the initial modulus of a fiber is not in a linear relationship with the strength of the same fiber; and the slope of tenacity *versus* initial modulus invariably increases with the increase of molecular mass.

Very similar results to those by Smith, Lemstra, and Pijpers were reported by

M. Kanamoto and co-workers.[41–43] From all of the reports quoted here transpires that the factors controlling the drawability are limited to the density of entanglements and to the number of tie molecules in the undrawn material. Also, in case of semicrystalline polymers the results of the drawing operation depend on the same factors. The latter of the factors is usually related to the prior one anyway. Kanamoto and co-workers[41–43] report also that in the case of two stage drawing, the drawing performance and the results depend on the same factors: the chain morphology, as well as on the crystalline morphology, of the undrawn material, in poly(ethylene terephthalate) in this case.

The amount of crystallinity in the predrawn material is equally important.[89] Not in all polymers is it as easy to obtain a low, or even practically non-crystalline material as in case of poly(ethylene terephthalate). Low crystalline material is easier to draw, more extensive draw ratios are possible and higher strength may be obtained. Also, the degree of crystallinity in such cases increases. Contrary to this, if the initial degree of crystallinity is high, upon drawing it often decreases. These results represent a confirmation of what was determined earlier by R. Bonart,[44] as is evident from figure X.11.

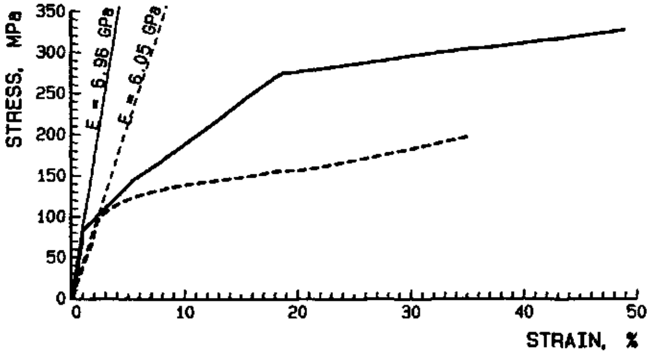

Figure X.11: *Stress - strain curves for poly(ethylene terephthalate) fibers: full drawn line: paracrystalline, room temperature drawn, low crystallinity, high modulus; dashed line: drawn at 125°C, higher crystallinity with relaxed amorphous regions, lower modulus. Quoted after R. Bonart.*[44]

In addition to the importance of the degree of crystallinity, or may be even more important, is the size of the crystalline blocks (along the a and b crystallographic axes).[44] The size of the paracrystalline blocks determines, to a large extent, how many *link molecules* will be formed. The link molecules are formed mostly from the polymer chains on the peripheries of the crystalline blocks, and for the smaller blocks, the ratio of the circumference to the volume of the block increases. Besides, clearly mechanically, the smaller units are easier to relocate, also, they lead to a better distribution of tensile force. With increasing number of link molecules, the strength, and possibly modulus, increase.

How can the important features of morphology in undrawn fibers be regulated? Degree of enchainment depends on the molecular mass, and therefore tenacity potentially increases with molecular mass. However, the degree of enchainment may be influenced by a balance of shearing - relaxation processes, and therefore so much space is devoted in this book to this and related topics. The size of crystallites is found to depend on the crystallization rate during fiber formation.[49] The shorter the total time of crystallization, the larger the sizes along the *a* and *b* crystalline axes. The slower the process of crystallization, the smaller crystalline blocks are formed. This has been known for long time; a slow formation process produced material which was easier to draw and better properties could be obtained.

It is necessary to remember that there are no miracles; increase of axial modulus is invariably connected with corresponding decrease of the modulus in the direction normal to the fiber axis. This principle is very well depicted on the diagram of the macroscopic modulus of fiber elasticity in relation to cold draw ratio published by Rauman and Saunders.[50] This diagram is reproduced in figure X.12. The diagram is a result of studies of unidirectionally stretched film of polyethylene. The authors stress that the result of drawing depends on orientation of both the crystalline and the amorphous phase; the properties of both phases are oriented likewise. The relatively very small values of the modulus in the direction of 45° to the direction of drawing are worthy of being remembered.

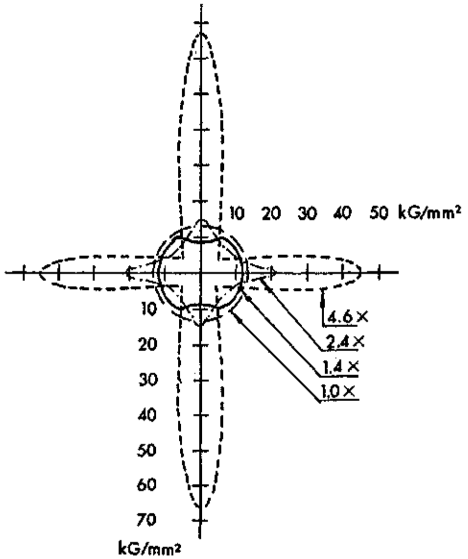

Figure X.12: *Macroscopic modulus of elasticity in relation to the ratio of cold drawing as obtained for polyethylene film. A polar diagram after G. Rauman and D. W. Saunders.*[50]

Another aspect of tensile properties is the mechanical stability of the fibers, or otherwise its succeptibility to creep. The creep in fibers is mostly considered as a negative property, and something to keep at the lowest level possible. High crystallinity, low modulus, and low orientation favor creep resistance, particularly the unrecoverable creep deformation.[38,44,51] Other factors diminishing creep are a higher molecular mass and polar character of the polymer chains. Darlington and co-workers concluded that essentially every aspect of fiber structure has an influence on creep.[53]

Higher modulus leads to higher creep. Higher modulus may be easier obtained when the fiber is drawn with neck at a lower temperature, closer to the glass transition, though not below it. And also the lower the temperature of the plastic deformation, the higher the succeptibility to creep.[45,53] And all this is in agreement with what was said before. Namely, lower crystallinity in drawn fibers favors high modulus[44,90], but stability (creep resistance) is favored by a high degree of crystallinity, provided that all other elements of structure are equal. As Darlington and co-workers found,[53] one should not even attempt to compare fibers of the same draw ratio, if drawn at different temperatures. In effect, one needs a compromise. Among two fibers with the same modulus, the one drawn at higher temperature will have lower creep. If possible, it is better to regulate the modulus not with temperature but rather with other means.

At this point it is necessary to mention another preference, if the fiber quality is of high interest. The closer a fiber is drawn to its maximum draw ratio the more stable is its structure, including a low creep. If a fiber is *incompletely drawn* then it may be more or less easily deformed additionally, despite the structure stabilization by the time factor, otherwise called aging.[52] Ideally then, a fiber ought to be drawn to its practical maximum, without incurring excessive breaks in the neck drawing. If a fiber of lower modulus is required, *e.g.* for soft and pliable apparels, the maximum draw ratio ought to be reduced by adjusting the formation process so to develop an appropriate structure in the undrawn fiber.

It is necessary to underscore that an increase of elongational strength and modulus is accompanied by a decrease of transverse strength. The better the fibrils are defined, the more stretched are the link molecules, the smaller is the cohesive force between the stretched molecules and between the fibrils.[89] The first and most obvious casualty of a low transverse strength is low abrasion resistance and peeling. By nature of polymers both high axial and high transverse properties cannot be had. High performance fibers are an example for this. Thus there are choices that must be made.

X.2.b Thermal Properties

As repeated many times earlier, the melting point of polymer crystals is not a material constant, it depends on the temperature of crystallization and solvent, if present. The prevailing mode of crystallization taking place during fiber formation is crystallization under strain, where the same rules are valid.[54] Additionally, it must be taken into account that crystallization during fiber formation, with the exception of some wet formation processes, does not proceed isothermally. Subsequent cold drawing is most often performed at more or less elevated temperatures rather than cold. In effect, fibers contain crystals of a wide range of long periods and the corresponding broad melting points.

The range of different melting points depends on the crystallization profile which results from the interrelation of the temperature profile and the profile of accumulation of unrelaxed work. The latter profile depends on the elastic character of the polymer melt or solution, it is on the polymer succeptibility for the acceleration of crystallization by strain. If a polymer crystallizes "sluggishly", then the spun fibers have low crystallinity and some fraction of the polymer may crystallize during the neck drawing. If the fibers are drawn in a step separate from the formation, a secondary crystallization may take place during storage, and this means crystallization at more or less room temperature, which indicates low melting. In such cases the subsequent neck drawing may determine the final melting profile to a much greater degree than it would otherwise.

During cold drawing, the entropy of the noncrystalline fraction is reduced, which may be observed in small changes of melting point (equation IV.75). As a result of annealing, the stretched noncrystalline chains may retract to some degree. The degree depends on the temperature of annealing, and also on the temperature of the cold drawing. Relaxation during annealing is specially strong when the temperature of drawing was lower than the temperature of annealing. The last phenomenon does not have a full and plausible theoretical explanation, though encountered experimentally many times.

Fibers in use are often exposed to elevated temperatures, apparels are laundered, technical fabrics often work at elevated temperatures too. Elevated temperature causes the same effects as annealing, and mostly it is annealing without any, or little, dimensional restrain. Fibers must have some dimensional stability and the stability may be regulated by the thermal history, the crystallization profile, and by the drawing history. As it was sketched here, the ways to produce thermally stable fibers are rather complex, but regulation is possible. Naturally, post-production improvement is possible through annealing under dimensional restrain. This does have the advantage that it may not only increase the thermal stability but also pre-shrinks the material, which may be welcomed by the user.

X.2.c Sorption Related Properties

Besides the tensile and thermal properties, there are other important attributes: dyeability, water absorption, swelling. Despite the fact that all these properties are strongly related to the nature of the polymer molecules, they may be influenced by altering the super-molecular structure in the solid state.[55–60] Naturally, when a polymer, *e.g.* polyolefin, is incapable of absorbing water in quantities which may have a practical significance, any changes of the supermolecular structure cannot increase the absorptivity. When a polymer has a potential for sorption, then the changes of fiber morphology will influence the degree and kinetics of sorption.

Fluids or dyes may be adsorbed on the surface, but they may also diffuse deep inside the fibers. Adsorption on the surface is limited by the size of the surface, and diffusion inside is normally the slowest of all processes involved. As the slowest process, diffusion determines the overall rate of a complex process, like swelling or dyeing.[61] Since all fiber structures are anisotropic, it is natural that the diffusion rates are different in different directions, which is described by the following equation.[62]

$$\frac{\partial C_A}{\partial t} + \frac{\partial C_B}{\partial t} + \frac{\partial C_C}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + D_B \frac{\partial^2 C_B}{\partial x^2} + D_C \frac{\partial^2 C_C}{\partial x^2} \tag{X.6}$$

where C_A, C_B, C_C are numbers of molecules of diffusant per volume of the media which are present in the crystalline phase, amorphous phase, and vacuoles, respectively, and D_A, D_B, D_C are effective diffusion coefficients in the crystalline phase, amorphous phase, and in the vacuoles, respectively. Crystalline lamellae are basically impermeable[60], which means that $D_A = 0$. Consequently, diffusion in a fiber depends chiefly on the diffusivity in the amorphous phase and in the vacuoles. But there is one additional factor to be considered: κ, the influence of the tortuosity of the diffusion paths. The diffusing molecules must execute a "slalom" between the crystalline segments of the fiber structure. The coefficient of tortuosity may be determined from

$$\kappa = \frac{\bar{D}}{D_B} \tag{X.7}$$

where $\bar{D}$ is average diffusion coefficient in fiber. In practice, κ may be found from a plot of $\bar{D}/D_B$ *versus* the volume fraction of the crystalline phase in the fiber. Attempts to describe the structure factor quantitatively in relation to the measurable structural characteristics have not led to success yet.[62]

Another way of determining the diffusivity is based on the measurements of the glass transition temperature changes in relation to a solvent content.[63] More details on this topic are to be found in section VII.2.

Dyeing of fibers is one of the areas heavily dependent on diffusivity. Nonetheless, the diffusion of dyes depends on the polymer and its morphology as well as on the affinity of the dye molecules to the polymer chains. The stronger the dye adsorbtion on the surface of a polymer chains, the more permanent the molecule location within the fiber, the more difficult it is for the dye molecules to move around. The diffusion of dyes depends also on the size of the dye molecules or on the size of the molecule agglomerates in cases of disperse dyes. The size of the dye molecules is often larger than the available interchain distances in the amorphous phase, particularly if the fiber was highly drawn. In such cases, dying technology resorts to widening of passages through swelling of the fiber structure. Since the majority of fibers do not swell in water, or they swell insignificantly, *carriers* are used to swell the fibers gently, to help the dyeing process.[61,64] The carriers are removed from the fiber, the swelling recedes and the dye molecules remain clenched and trapped within the fiber structure.

Aside from the nature of the polymer chains and any physico-chemical interaction between the polymer and the diffusant, sorption depends strongly on the level of crystallinity and on the morphology. The diffusivity along the fiber radius initially increases with the draw ratio to reach a maximum at the draw ratio of about two. With the draw ratio increasing further, diffusion decreases again. The diffusivity along the fiber axis decreases steadily with increasing draw ratio, without any maximum, and always is smaller than the diffusivity in the radial direction.[65–67] Thus, the orientation effect, rather the density increase connected to it, has a very strong influence on the diffusivity, even with the unchanged level of crystallinity.

Annealing initially causes a decrease of diffusion of dyes; after the diffusivity reaches a minimum, it increases again. Conditions of the annealing determine the location of the minimum of adsorption.[68] Diffusion of solvents, and its ultimate stage – solubility, changes in an analogous way.[69]

Dyeing is a two way process, the fiber morphology influences absorption of a dye, and presence of a dye in the fiber influences the fiber properties. The latter influence is small since the relative amounts of dyes are normally very small. When there is a necessity for the polymer molecules to undergo some realignment to accommodate the dye or other molecules, then this is connected with some change, usually an increase, of entropy.[70] Should the amount of dye or other material absorbed be larger, then the chain mobility may be restricted by the absorbed molecules. Whatever the dye uptake, degree of swelling, etc., presence of the " foreign" molecules finds a reflection in some change of the glass transition temperature.[71]

If the nature of the polymer allows adsorption of water or other solvents, then the adsorption proceeds according to the same rules as in the case of dyeing. There may be, however, quantitative differences related to the size of molecules; dye molecules are usually fairly large, while water and solvents have small molecules. The small molecules may be easier, or in larger quantities accommodated within the fiber structure.

X.2.d Fiber Uniformity

Uniformity of fiber diameter almost always belongs to the crucial parameters determining the product usefulness and quality. The uniformity of fiber diameter is related to the uniformity of the fiber morphology along the fiber axis. Uniformity, as a strong determinant of the fiber quality, represents an important economic factor. Thus, fiber uniformity is a matter of constant concern in the fiber manufacturing. The importance of securing uniformity in commercially produced fibers, along with the complexity of the problem, may well be the reason for the scarcity of publications in the field. General experience teaches that fiber nonuniformity may originate from many sources and reasons which may disturb the stability of the process. The analysis of fiber formation processes presented here gives sufficient indication of the extremely fragile nature of the process. The teachings of experience are in agreement with this. That is, probably, why fiber formation is still called an art. This section presents only the more important points concerning uniformity, the subject is mentioned often in other chapters.

One of the more common sources of nonuniformities in fibers is inhomogeneity of polymer.[72] Accidental mechanical impurities, lumps of cross linked (gelled) polymer, lumps of degraded polymer[73] belong in this category.[74] The character of the polymer determines, to a large extent, the character of the impurities, *e.g.* its thermal stability, tendency toward cross linking, general efficiency of the polymerization catalyst as reflected in the chain abnormalities, etc. Poorly designed transfer lines, *e.g.* dead spots, constitute good conditions for generation of degraded polymer. It is self understood that the best remedy here are good, efficient filters. In some polymers, presence of gel is unavoidable. High shear rate in the filters, though still below the shear degradation of the matrix polymer, may be able to degrade, at least partially, gelled polymer as its molecular mass is high so its degrading shear rate may be well below the applied conditions.

It is self understood that extrusion from the spinnerette cannot result in a fractured flow. Narrow entry cones and relatively long capillaries are to be recommended here (see sections III.6 and III.7). Generally, it is not good to operate on steep slopes of die swell *versus* capillary length; small inaccuracies in the the capillary dimensions may increase fiber-to-fiber nonuniformities, and further they may cause differences in the degree of extension of the melt. Inaccuracies in the capillary drilling, minor changes in diameter, influence shear rate to the third power, and this may create conditions where some of the filaments will be closer to the critical shear rate than the other.[75]

The most sensitive area of the process is, without any doubt, the quench (or coagulation) zone. One of the most obvious reasons for nonuniformities is the presence here of an excessive drawing force (or speed, or initial stress on die swell). If the extension rate reaches a critical level, the extrudate becomes nonuniform.[76] If the extension is close to the critical value, any fluctuation in quench intensity may cause the flow to fracture intermittently, all this leads to uneven diameter.

As mentioned earlier, the segment of filament path where the polymer crystallizes almost always shows some signs of instability. The true reason for this is not known, though one may consider that a phase transition is by its nature a kind of instability. However, the question "why?" and "when?" about that instability cannot be answered yet.

Even greater potential danger of instabilities exists when at the end of the crystallization process the filament is still physically in the quench zone; when under the influence of high forces the cold drawing begins. In some commercial processes exist such, or similar, situations. Invariably there is a danger of diameter nonuniformities, at least intermittently. This danger increases with the increasing drawing force, which is often typical in formation of fibers for spunbond fabrics. (See chapter 11.)

Vibrations of the machine are easy to transfer to the filaments; contemporary high velocity transporting rollers may be quite capable of causing such vibrations. Turbulent flow of the cooling medium may cause similar effects.[80] All sorts of vibrations, or filament fluttering, cause periodically variable tension and this may be the cause of periodic uneven diameter attenuation of the formed fibers. This, in turn,may lead to small fluctuations in the development of structure, leading to uneven drawing, which results in diameter variations. The cycle of cause and effect becomes closed. The variable diameter, and especially the structural variations, may lead to the formation of excessive differences in the local drawing ratios and to relatively large fiber unevenness in the cold drawing step.[46,81]

Uneven diameter may cause uneven heat exchange in the point of neck down. If so, then this would result in local variations of the draw ratio. Nonuniformity of quench may have very similar symptoms as vibrations,[72] and this may complicate the diagnosis of a case.

If the rollers are incorrectly designed, the filaments may slip on the surface of the drawing rollers, and this is another very obvious cause for generation of nonuniformities of fiber structure and diameter.

One has to take note that practically all conditions leading to filament nonuniformities result in a variable spinline tension[77] and velocity, so the tension, and/or the corresponding filament velocity measurements represent a primary diagnostic tool. Comparison of the tension in drawing zone with the tension in quench zone may help localize the point where the nonuniformities arise. Experience permits one to distinguish between some of the nonuniformities from the character of the tension and velocity fluctuations.

Depending on the structure of the undrawn fibers, there appears to be an optimum range of drawing temperature which is most favorable also for fiber uniformity.[77–79] Periodic stress oscillations and the resulting diameter changes have been noticed during drawing operations.[79] The conditions for such oscillations to take place appear to depend on the rate of deformation and on temperature inside the neck, as well as on the compliance of the sample. In this case the compliance has been defined in a somewhat unusual way: it is the change in the length of the sample divided in the stress causing the change.[79] Although in the original work, the experiments were carried out in the vicinity of glass transition temperature, the conclusions may very well be valid under other temperature conditions too. The conclusion that follows here immediately is that the length of the drawing zone must be adjusted so as to operate at low values of compliance, as defined here. Especially dangerous is the high range of possible temperature, as filaments may occasionally stick to the hardware.

The nonuniformities created in various stages of the process will be transmitted down the threadline. Therefore, the higher up in the process line the instability occurs, the more dangerous it is. But, contrary to the intuitive expectations and to some opinions,[82], neck drawing may sometimes improve the fiber evenness over that present in the undrawn fibers. When the fibers are cold drawn under proper conditions, some types of the nonuniformities generated in quench (or coagulation) zone may be diminished or outright eliminated. As an example: small temperature variations would lead to changes of rheological properties; the hotter segments may be extended more and at higher rate, which may eventually lead to an increased crystallization rate at higher temperature. As a result the thinner segment may be cold drawn less than the neighboring segment, initially thicker but possessing a crystalline structure more apt to the plastic deformation. Nevertheless, such a "self-improvement" of uniformity is not a rule to depend on; if it happens, it is rather a "patch up" by way of a good luck. It is highly unlikely to obtain perfectly drawn fibers from poor quality undrawn fibers.

X.2.e A Summary

Simultaneously as a summary and as a quick reference, the trends in changes of the neck drawing performance and of the resulting fiber properties are given in table X.4.

Table X.4.
DRAWING PERFORMANCE IN RELATION TO FIBER PROPERTIES

PROPERTIES OF UNDRAWN FIBERS	DRAWING PERFORMANCE				PROPERTIES OF DRAWN FIBERS				
		MAXIMUM							
	DRAWING TENSION	DRAW RATIO	TEMPERATURE	DRAWING RATE	CRYSTALLINITY	ORIENTATION	MODULUS	CREEP	THERMAL STABILITY
LOW CRYSTALLINITY	L	H	L	H	↑	H	H	H	L
HIGH CRYSTALLINITY	H	L	H	L	↓	↓	L	L	H
HIGH PRE-ORIENTATION	H	L	↑	L	↑↓	H	L	L	H
SMALL CRYSTALLITES	L	H	L	H	↑	H	H	H	L
LARGE CRYSTALLITES	H	L	H	L	↑↓	L	L	↑↓	↑↓

H Higher or high; L Lower or low; ↑ Tendency to be higher;
↓ Tendency to be lower; ↑↓ Illdefined result, complex relationships.

The conditions of a cold drawing process influence the properties of the resulting fibers. However, the range of applicable drawing conditions depends on the structure of the fiber entering the drawing stage. The information summarized in table X.4 underscores the obvious fact that in effect all fiber properties depend on the fiber structure. Any change of the fiber properties, if it is to be achieved, must be realized through alteration of the fiber structure, and the structural alterations must start from the development of the morphology of undrawn fibers and continue all the way through the end of the neck drawing. It is necessary to remember that drawing of a fiber to an extent much smaller than the practical maximum is, with few exceptional cases, ill advised.

And what makes the fiber formation processes so difficult and so interesting is the large number of different process variables. All of the variables must be carefully controlled throughout the process; this is needed to have a command over the development of fiber structure, which determines the fiber properties. The full understanding of the relationships is the main key to success.

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