I INTRODUCTION

I.1 Historical Background

The first *artificial fibers* were made toward the end of nineteenth century on the basis of natural polymers: cellulose and casein. The knowledge of fully synthetic polymers was at that time still highly inadequate.[1–5]

These natural polymers do not melt – they decompose at elevated temperature. This simple fact dictated the first methods of fiber formation. The polymers, or their modifications, could, however, be dissolved. In solution form the shape of the materials could be changed, and by subsequent solvent removal the shape could be fixed. On these principles were based the first patents protecting fiber formation.[6–9]

Cellulose does not dissolve easily in any of the commonly used solvents of that time. Later, the choice of solvents for cellulose was extended by the addition of cuprammonium – a substance not very pleasant to work with. The realities of difficult solubility led to the development of another way to prepare solutions: namely through formation of cellulose derivatives: nitrocellulose and cellulose xanthate – a product of reaction between cellulose and carbon disulfide. In the case of xanthates, immediately after shaping the solution into fibers xanthate was regenerated back to cellulose. This became known as the rayon process, which, with many refinements, is still in commercial use.

There are two applicable ways to remove the solvent: evaporation or extraction. Thus the processes which today are referred to as dry spinning and wet spinning , or more correctly as dry or wet fiber formation, were born. In the former, the solvent is removed through evaporation, while in the latter the solvent is removed through extraction, with or without a chemical reaction taking place simultaneously. In both of the methods diffusion plays the key role. The rayon process involved a chemical reaction to regenerate the cellulose, thus it was limited to a wet treatment for the sake of the reaction, as well as for an extraction of the byproducts.

With continuing progress in the area of synthetic polymers, thermoplastic polymers eventually came under consideration for fiber formation. The thermoplastic nature of the polymers allowed the omitance of solvents as a processing aide, but extrusion and further processing of the highly viscous melt brought new problems. These were reflected primarily in new demands on hardware. The higher viscosity of polymer melts and larger emphasis on the attenuation of the fiber diameters necessitated the involvement of the science of rheology; problems connected with fiber formation became for rheology an important field of research.

In the past the three methods of fiber formation – dry, wet, and melt spinning – were treated as entirely different processes having very little in common. From an operational point of view, this opinion may be justified to some extent. Indeed, from theoretical and technological points of view, these processes are very similar.

Schematic representation of fiber formation by all three main variants of the process is given in Figure I-1. To begin with, the dry polymer is either melted or dissolved, possibly after a modifying reaction. While the polymer melting is continuous in screw melters or extruders, or fed directly from continuous polymerization units, dissolution is performed in batches. In the old days melting was accomplished on grill heaters located closely to the spinning blocks. In any of the cases, the polymer solution or melt is transported to spinning blocks. The necessary pressure is delivered either by extruder, as in contemporary melt spinning, or by compressed gas (nitrogen), as in spinning from solution or grill heater melted polymer.

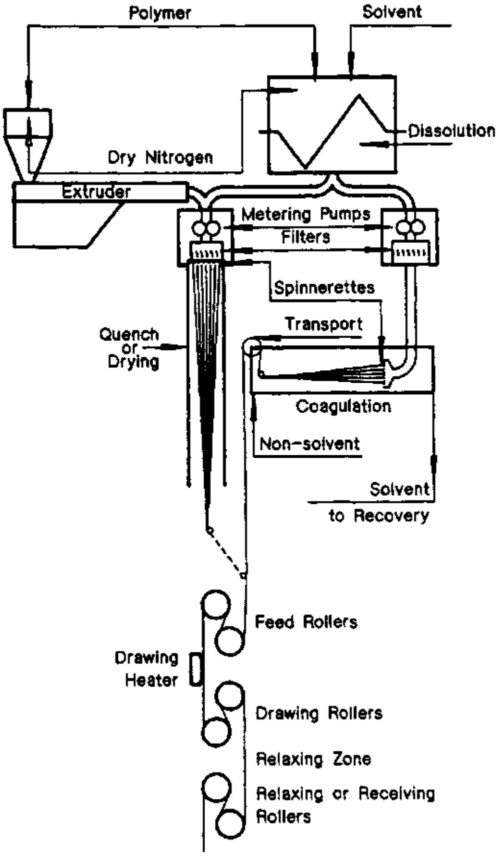

Figure I.1: *Schematic representation of the fiber formation process.*

The spinning block is equipped with a cavity for a fluid metering pump, and channels which lead the polymer melt or solution to another cavity, where the filter and spinnerette are located. The spinnerette is a metal plate, sufficiently thick to withstand the pressure gradient and equipped with a multitude of capillaries through which the polymer or its solution are extruded. The block must be equipped with means for rigid control of temperature.

In the case of wet formation processes, spinnerettes are not mounted in the spinning block but on transfer tubes which allow the spinnerettes to be submerged in the coagulation bath or located few millimeters above the fluid surface.

So far, for all three formation methods, processing is quite similar. Some differences begin from this point on. The purpose of the treatment of the extruded stream is the same in each method: to solidify the polymer. The means of accomplishing this goal vary with each method and constitute the main point of differentiation.

When a molten polymer is extruded through a capillary it will solidify on cooling. The cooling medium may be gas or liquid. If a stream of polymer solution is extruded into a gas atmosphere the solvent may be removed only by evaporation, the heat of evaporation must be delivered by the gas. In the wet methods the polymer stream is extruded from spinnerettes submerged, or almost submerged, directly into a fluid which extracts the solvent from the filaments. If a chemical reaction accompanies the process, the course of events is more complicated. In regenerative processes the polymer is regenerated, it becomes insoluble – it coagulates – and phase separation occurs. Polymer may also be synthesized from precursors, or may be cross linked by the coagulating baths which render it insoluble. The diffusion processes are temperature dependent, so the coagulating bath must be well thermostated. In case of chemical reactions taking place in the coagulation bath, temperature control may become more complex due to the heat of reaction. Extraction by itself does not involve significant thermal effects.

In the case of formation from solution, the solvents and nonsolvents used must be recovered for economical, as well as safety and ecological reasons. The prevalent method of solvent recovery from the gas is by adsorption on activated carbon, with subsequent steam regeneration of the carbon bed, and separation of water and solvent (distillation). This method of regeneration is quite expensive. In cases of wet method, usually only distillation suffices; this method may be more economical, particularly if the solvent is more volatile than water.

Many industrial operations are interrupted at this point. Fibers obtained in wet processes at this point may require washing, and certainly drying. If dry formation is done using relatively high boiling solvents, the formed fibers may also need additional washing to remove residual traces of solvent. Another reason to interrupt the operation here may be crimping and/or heat treatment processes, which may proceed at a different rate than the formation itself. Besides, crimping is usually done on dry fibers, or with steam, under controlled moisture level. There are, however, many operations where the fibers are subjected to plastic deformation (neck drawing) in one line with the formation process.

The process of polymer solidification is quite complex. The majority of the polymers used for fiber formation do form a crystalline structure. The crystallization process usually takes place simultaneously with the solvent removal or due to decrease of temperature of the melt. Slower crystallizing polymers have only large viscosity increase due to the cooling of polymer melts, crystallization process takes place in further steps. It is quite understandable that the crystallization process proceeds differently, depending on the temperature change, presence or absence of a solvent. Besides the phase and temperature changes, the filament diameter is attenuated by stretching . And all that at the same time! The stretching is necessary as it is essentially impossible to extrude the filaments at their final thickness. For this reason one extrudes as small a diameter as practical for all possible reasons, and then the filaments are extended while still molten or still containing enough solvent. The large number of processes and events taking place simultaneously in the relatively small space and very short time contribute to the immense complexity of the whole problem of fiber formation. This complexity of quench, drying, and coagulation zone creates the greatest obstacle in unraveling the different phenomena, in developing a complete and sufficiently accurate theoretical description of the whole process, as well as difficulties with the understanding of the nature and the essence of the process.

The formed, undrawn fibers ("spun fibers" in the industrial slang), which have been washed and dried if necessary, do not have good physical, and particularly tensile, properties. Very early in the history of fiber making it was discovered that the fibers as formed may be permanently deformed by a relatively low stretching force. Such stretching results in an increase of the tensile strength. Therefore, almost all fibers, irrespectively of the method of their formation, are subjected to such a deformation. The stretching operation is usually carried out by transporting the fibers through rollers driven at different surface speeds. In Figure I-1 the rollers are identified as feed (or take up) rollers and drawing rollers. From the point of view of crystalline morphology of fibers, the stretching corresponds to plastic deformation; it is often called "neck drawing" due to the characteristic abrupt diameter change, which resembles a bottle neck, or simply the drawing. The plastic deformation is usually performed at elevated temperature, though below the onset of melting of the crystalline structure. After the stretching operation, the fibers may show a tendency for some recovery. It is advisable to let them recover under controlled conditions: to add a pair of relaxing rollers rotating at appropriately lower velocity than the drawing rollers.

Depending on the polymer and process used, and on the type and quality of product intended, the drawn fibers may be subjected to various finishing operations: washing, heat setting, winding on bobbins, or cutting for staple.

There is another finishing operation, which is not necessarily performed at the end of the manufacturing line. These are finishes applied for different purposes: to facilitate drawing and/or crimping, to prevent electrostatic charging, and almost always to improve textile processing . Depending on the type and the purpose of the treatment, the finish may be applied at different stages of the manufacturing line.

The above description of fiber making is brief and highly simplified. It is to serve as a starting point for detailed discussion of all the essential phases and the phenomena taking place during the process, and as the initial vocabulary or bridge for communication with the reader. The scheme given above concerns only the manufacturing of the classical fibers and disregards some newer methods and products. Some of the newer processes, raw materials, and products, such as polymer blends, bicomponent fibers, spunbonded materials, are treated in an abbreviated fashion, because the majority of the technological problems they involve represents only modifications of the basic principles of fiber formation. However, some of these problems will be given some attention since they represent either interesting solutions to problems, or a good example for the principles working in different processes, or because they have experienced commercial success

I.2 Nonconventional Formation Methods

As mentioned above, the fiber formation process is complex. This simple fact represents a strong driving force to attempt to simplify the technology. The always present need for the reduction of manufacturing costs reinforces the drive toward new and simpler formation methods. The initial efforts have been concentrated on attempts to eliminate the roller type transport of fibers and spinnerettes as expensive pieces of high precision hardware.

The first known attempts to eliminate fiber transport rollers in fiber formation from polymer solution date back to 1934. In place of rollers between the capillary and collecting device, an electrostatic field of 50 to 300 kV was applied.[11–14] Such a process usually bears the name of *electrostatic spinning.*

Spraying of a polymer solution, or melt, by means of high pressure and high velocity air[15–17] represents another technique leading to similar results. Extrusion of polymer melt through a long slit type die was still another method leading to the same general goal. The extruded filaments may then be extended in a Venturi type jet with high velocity gas. Such jets are able to provide the necessary extensional force. This group of methods is normally referred to as *spray spinning.*

In another attempt to eliminate the spinnerette, a process has been developed where a polymer solution or melt is introduced axially to the center of a rotating cone or bell. The centrifugal force distributes the fluid over the internal surface of the bell into a film of progressively decreasing thickness. When the film leaves the edge of the cone, the film splits into fibers. Solidification takes place by the way of drying or cooling. The centrifugal force is sufficient to extend the fibers to as fine diameter as fractions of denier*.[19] Such a process bears the name of *centrifugal spinning.*

There exists a process which combines centrifugal and electrostatic forces. The centrifugal - electrostatic processes find an application mainly to manufacturing of spunbond fabrics.[20,21]

Another group of nonconventional processes concentrates on facilitating melt processing of high molecular mass polymers. All of these methods invariably "dilute" the polymer with solvent what lowers the viscosity to various degree. The

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*Denier, den or dpf, is a measure of mass, or weight, titer; it is the weight of a filament of the length of 9000 meters. A "metric" mass titer is tex, Tx, the weight of a 1000 m long filament. The "decitex", dTx, is most often used.

solvent selection represents a crucial point in those processes. In some cases solvents are selected so that they become non - solvents at lower temperature and/or pressure. In some cases the solvent violently evaporates when the extrusion pressure ceases upon leaving the spinnerette. Yet another processes, aimed at obtaining very high strength and high modulus fibers, extrude the polymer only swollen by the solvent to a state of gel.

All of the nonconventional processes are governed by the same laws and principles as the conventional fiber formation methods. On the other hand, all of the nonconventional processes seem to have some deficiency, none of them is ideal. The most common fallacies are: nonuniform fiber diameter, both fiber-to-fiber, and/or along the fiber. For the majority of the processes without spinnerettes it is virtually impossible to subject the spun fibers to cold drawing (plastic deformation). Generally, only certain products or raw materials, which do not require plastic deformation at all, or only to a modest extent, are suited for such processes, e. g. elastomers. Some spunbonded processes, mainly for disposable products, where dimensional stability of the fibers and higher tensile strength are not required, utilize the nonconventional methods. The inherent deficiencies of the nonconventional methods are serious enough to prevent, or seriously limit, application of the products as traditional textile fibers for apparels. Some of the semimelt processes yield high class fibers, but the high price limits their application to very special purposes.

I.3 Traditional Understanding of the Process

Development of new technologies is often done by *trial and error*. The technology of fiber formation went through a similar period. Moreover, that period lasted longer, relatively speaking, due to the complexity of the physics of the unit processes involved and the extraordinary many simultaneous and interrelated unit processes involved. It is well known that trial and error approaches usually result in an abundance of errors, but every new inductive science must go through such a difficult childhood. By now, the technology is over hundred years old. During all that time, a great wealth of observations and experience has been accrued. Alas, the majority of this knowledge has not been published. The commercial significance of fiber manufacturing explains the hesitation in the publication of anything that may prove important. This was particularly true of the initial trial and error period. Nevertheless, as fiber formation has gradually obtained the rank of science, more and more information has found its way into scientific journals; though sometimes with substantial delay. [22-30] As a result of the specific spirit of secrecy in which the fiber industry has placed itself, the fiber makers and the fiber making procedures have became surrounded with a peculiar aura of an art, if not a black magic.

During the long studies of the raw material - process - product relation, it was established quite early that despite the most scrupulously held constant polymer properties, small changes in processing may cause "unduly" severe changes in the product properties. Similar sensitivity of process - product relations were known in metallurgy, but never to such a significant extent. In metallurgy, the majority of such changes could be ultimately related to some minute variations of chemical composition or to the crystalline polymorphism, or both. Gradually, with time it became evident that, by their nature, macromolecules usually do not attain thermodynamic equilibrium.[31] The large chain-like molecules assume a multitude of different conformations depending on their thermal history and history of their mechanical perturbations. Because of the lack of more accurate knowledge, the thermal history was held responsible for everything, particularly for everything bad, that could happen. The lack of a sufficient explanation and of a well grounded understanding did not allow to lay a firm theoretical basis for fiber production. Empirical formulations and "the rule of thumb" became the last resort. On the basis of mainly qualitative observations of different processes, a number of *"iron rules"* for fiber formation have been gathered.[32] They are:

- Narrow molecular mass distribution in a polymer facilitates the processing and generally improves the product properties.
- Increase of shear rate in the spinnerette increases the fiber tenacity.
- Increase of the spin stretch usually increases the crystallinity of the formed fibers.
- Tension in neck drawing, at a given draw ratio, is proportional to the crystallinity in the undrawn fiber.
- Maximum crystallinity that is obtainable in the drawn fibers depends in inverse proportion on the degree of crystallinity present immediately before the neck drawing operation.

Aside from the simplistic form, these rules represent an immensely significant basis for the past development work, and they may still be helpful to understanding of the many results published under the headings of "surprising". But it must be also realized that the experimental verification of some of the points, although performed many times over, represents a difficult task. Proper separation of different variables is of utmost importance. In every formation process not all of the variables are individually and independently adjustable. Modern testing equipment allows the measurement of the spinline conditions,[33,34] thus it has simplified the verification of those qualitative rules. More importantly the equipment provided a firm basis for the modern quantitative description of the process. In view of the quantitative information, some of the *"iron rules"* were found to need qualifying footnotes.

Aside from their historic significance and practical importance, *"the iron rules"* describe the process neither completely, nor even adequately. Fiber formation is one of the most complex processes the chemical industry has ever dealt with. Therefore, one cannot expect it to be described sufficiently by only a few "rules". Despite the unquestionable progress, at this moment there are still no full and complete quantitative solutions available. The fully quantitative scientific predictability is still limited since several of the fundamental problems in polymer physics have not been solved yet.[31]

I.4 Newer Theoretical Approaches

In the early 1950s, work began on a more scientific approach to fiber formation. Earlier, products and processes were invented, studied, and developed only by chemists and engineers. The newer approach in fiber research involved many physicists.[35–37] One may distinguish two different methods characteristic to those efforts.

In one of the approaches, the exploratory work was carried out on certain aspects of product or process. Usually the studied problems were selected so to cover a very narrow area of specialization, often limited to using only one experimental technique. Some of the investigations of this kind produced much valuable data. Some of these studies of the *unit processes* were deep indeed. However, the isolated conditions sometimes put limitations on the general validity of the interpretations. The experiments were simply too much out of context in relation to the entire process. In studying literature of that period, it is often necessary to reevaluate and reinterpret the published conclusions. Taking into account the principles of the methodology of sciences,[38] such studies of isolated aspects may be justified, provided that the potential dangers of premature generalizations are heeded, so that misleading conclusions are avoided.

As the first approach was predominant in more "descriptive" areas, e.g. fiber structure, the second one involved attempts of quantifying the process. With sufficient fairness one may credit E. H. Andrews[35] as its originator. Many quantitative descriptions of great value have been obtained, though unfortunately, not always were they immediately applicable in practice. As an example one may quote the Andrew's solution of heat transfer equation,[35] which gives good results in case of non-crystallizing polymers. Since the process of polymer crystallization under strain had not been solved at that time, it was a scientific distortion to put the large heat of crystallization at an arbitrarily chosen point of the spinline. A certain dose of impatience and underestimation of the process complexity can be detected in some of the interpretations and conclusions assigned to these otherwise substantial achievements.

The quantitative descriptions of the unit processes involved in fiber formation pose calculational difficulties, only a small fraction of them may be solved analytically. In recent years the application of widely available, potent, and fast computers to cope with the difficulties of the purely computational nature have placed the fiber formation technology where it is today. Computers allow a wide use of numerical methods and simultaneous solution of systems of equations. In this way, today the fiber formation process may be fully quantitatively defined only with the necessity of experimental analytical support.

The full development of fiber formation technology, that is, to the point of total quantitative predictability on the basis of laboratory analyses, is still incomplete. The full predictability of the process appears to depend mainly on the filling of the gaps in polymer physics. It is also imperative that the future research endeavors be undertaken so that the complexity of the whole process be considered and respected both in its theoretical and experimental aspects.

On the other hand, we must be grateful to past researchers for the development of the starting points. After the thorny beginning, compilation of the available methods, proper reinterpretation of them, provided a strong base for the current state of knowledge in the field.

In the following chapters, all theoretical treatment of the unitary processes and phenomena involved in fiber formation and available today will be given separate accounts. Simultaneously, the theories will be confronted with the wealth of the available experimental evidence. The analysis of the mutual relationships and influences between the unit processes involved in fiber formation plays a crucial part. The available quantitative descriptions and their agreement with experiments – *ergo* their applicability will be ascertained. The different aspects of the process will be brought into one entity: into a logical system of fiber formation science, as it stands today. Though some areas of polymer physics still require solutions, the amount of confirmed information already gathered, when logically assembled, permits the fiber formation technology to be rightfully called the **fiber formation science**.

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