VIII PROCESS VARIABLES

In fiber formation processes, the variables responsible for process control are not as obvious as is the case of many of chemical processes. On the other hand, the large number and the complicated character of variables is responsible for the complexity of the entire process.

Normally, in chemical technologies we have to deal with three different types of variables:[1]

- Theoretical variables

- Technological variables

- Operational variables

Theoretical variables deal with the most important properties of the raw material and the necessary changes the material must undergo to be transformed into a fiber.

Technological variables take into account the theoretical variables and the requirements imposed by the particular process used. The *"what we are doing"* is more than often influenced by the *"how we are doing it"*. Polymer processing may be bound by this principle to more than an average degree.

Operational variables result from the superposition and interaction of the technological variables with the equipment used. Since there is almost an infinite number of solutions in the equipment design, a limitless pattern of knobs and switches, operational variables cannot be generalized, and in consequence, they will not be discussed further here.

The quantitative justifications, if available, were given for the most part in the previous chapters. The discussion of the process variables contained in this chapter is intended to introduce some organizational and systemic gradation of the different elements of the process. The large number of variables involved in fiber formation and their strong interrelationships seem to justify this kind of synthetic recapitulation.

The variables discussed here are related primarily to the "basic process", to fiber formation from the melt, as is the entire book. The small differences necessary to apply the system to the processes from solution are given in addition to the main concept. The possibility of such an organization of variables dictates that fiber formation ought to be considered as one process. Melt, dry, or wet processes are only variants of the "basic formation". In a similar way, the other, newer processes, like gel spinning and semi-melt spinning, may be considered as only variants of the basic principles.

VIII.1 Theoretical Variables

The process variable may be considered only with the understanding that the type of polymer, and possibly polymer-solvent, or polymer-solvent-nonsolvent system, as the case may be, is constant. With such an assumption, one may list the theoretical process variables as they are given below in table VIII.1.[1] The list of variables is followed by a list of the most important effects the variables have on the fiber structure, which in turn determines the fiber properties.

Table VIII.1

THEORETICAL VARIABLES IN FIBER FORMATION.

POLYMER, EXTRUSION, SOLIDIFICATION

- MOLECULAR MASS (DISTRIBUTION FUNCTION)
- CHAIN STRUCTURE IMPERFECTIONS
- CHAIN ENTANGLEMENTS (shear history)
- TEMPERATURE PROFILE *versus* TIME
- STRESS PROFILE *versus* TIME and TEMPERATURE
- PHASE COMPOSITION *versus* TIME and TEMPERATURE
- RATE OF SOLIDIFICATION *versus* TEMPERATURE

PLASTIC DEFORMATION - NECK DRAWING

- DRAW RATIO
- DRAWING RATE
- DRAWING TEMPERATURE

EFFECT ON FIBER STRUCTURE

EXTRUSION AND SOLIDIFICATION	*PLASTIC DEFORMATION*
CRYSTALLINE STRUCTURE	FIBER MORPHOLOGY
DEGREE OF CRYSTALLINITY	FIBRIL DIAMETER
SIZE OF "MOSAIC" BLOCKS (a -, b - axes)	FIBRIL LENGTH
LATTICE DISTORTIONS (g - factor)	NUMBER OF TIE MOLECULES
FOLD LENGTH (long period)	NUMBER OF LINK MOLECULES
NUMBER OF TIE MOLECULES	FROZEN STRESSES

Molecular mass, understood as the entire distribution of the molecular masses, describes all polymer properties. Viscosity function, relaxation and retardation functions, and the entire rheological behavior depend on the molecular mass and its distribution. The same is true of all the other properties related to phase transitions, solubility, etc., etc.

If we know the polymer, we know everything else that there is to know. However, there is one question to be asked: is the polymer really what we believe it should be?

Chain structure of polymers is not always what it is supposed to be; the sequence of monomer units in the chain is not always, and not in all individual molecules, reflected by the chemical structural formulas we write. Organic reactions are known to have incomplete yields, byproducts are formed. In the case of polymers, there can be no purification to remove the byproducts, as they are built in into the chains. The amount and distribution of the chain imperfections has an influence on polymer properties; sometimes the influences are small, outright negligible, sometimes they mean very much. Colloquially we speak of polymer quality, which often translates to the difference between one vendor and another.

Characterization of chain imperfections is difficult, laborious, and costly in the majority of cases. For this reason, in industrial practice the presence, or rather change, in the frequency or distribution of chain imperfections is only first noticed when "something goes wrong". It is this "something" which may be so difficult to determine but is always threatening.

It is obvious that deviation from a regular chain structure changes the material properties, behavior in processing, and thus the results of the process. The quantities of the imperfections involved are extremely small, a minute fraction of one per cent. The effects of those small quantities on product, and particularly on the process performance are usually disproportionately large. An effort invested in the determination of the structural purity is often time and money well spent.

Chain entanglements, may vary quantitatively for the same chains, depending on the temperature and deformation history. On the other side they introduce changes in polymer properties and behavior, and these changes are not necessarily subtle. There is no method known to "dial" the entanglement density, we may just try to maintain constant history of the material, on top of the constant purity. The structural deviations have a very strong effect on the chain rigidity, and this is related to the propensity for development of entanglements.

Temperature profile *versus* **time** belongs to the most obvious variables, it determines rheological properties of the polymer and the phase transition(s) involved in the structure development.

Stress profile *versus* **time and temperature** determines how the fiber diameter attenuates. The attenuation, in turn, is the main determinant of stress; force applied is constant and it changes relatively little along the way. Stress together with the temperature-time profile influences phase transitions.

Phase composition *versus* **time and temperature** has a particularly strong effect in solution processes, as it also determines rheological properties. In all processes it determines solidification and the resulting change of polymer behavior.

Rate of solidification *versus* **temperature** has a great responsibility for the quality and quantity of structural elements in the fiber. This variable is strongly related to the phase composition - time - temperature relationship; it may be outright derived from it. Despite the fact that this variable does not always have a simple relation to the profile of phase composition, the rate of solidification must be treated as a separate variable. Also, in cases of polymers which do not crystallize eagerly, the solidification may extend to the time outside of the formation machine.

The list of theoretical variables seems to describe everything important in the raw material and its transformation to obtain fibers of a desired structure; it describes the variables down to the most basic, most fundamental, elementary core. The fact that the number of technological variables is about three times as large speaks of the enormous complexity of the process.

VIII.2 Technological Variables

In a real process we have to create a situation which assures that the theoretical variables related to the raw material will be satisfied by the raw material used, and that the physical conditions and mechanical processes will create an environment which will satisfy the variables related to the processing. This is a rule in the general technology. By the time we determine all the variables needed to be under control for a process, the number of technological variables will be about threefold the number of theoretical variables. To facilitate the discussion we shall divide the variables into four groups: polymer system, extrusion, quench or coagulation, and drawing.

The subject is further complicated by a not entirely usual fact: not all of the variables can be changed at will. Thus we have two types of variables: *independent* and *dependent*. The independent variables may be changed at will within a technologically sensible range, for instance molecular mass of a polymer or extrusion temperature. There are, however, such properties, conditions or states which do have an influence on the course or the result of the process but cannot be regulated independently, like shear rate or profile of the filament temperature – these are the dependent variables.

A change of every independent variable causes alteration of at least one dependent variable, though it is usually more than one. The dependent variables, on the other hand, are usually affected by changes of more than one of the independent variables. Yes, initially it may appear confusing. Nonetheless, there is a logical system in this, almost like in a Cretan labyrinth. Table VIII.2[1] presents the technological variables and a sketchy, not very perfect scheme of the variable interdependence. Despite its imperfections, the table visualizes the far reaching effects of some of the independent variables; the higher up they are in the table the further down effects of their change reach.

Table VIII.2
TECHNOLOGICAL VARIABLES AND THEIR INTERRELATIONSHIPS

POLYMER SYSTEM																		
	MOLECULAR MASS FUNCTION	Δ																
	STRUCTURAL IMPERFECTIONS		Δ															
	PHASE COMPOSITION (CONC.)*			Δ														
	RELAXATION/RETARDATION FUNCTIONS	↑	↑↓	↑														
	SHEAR VISCOSITY FUNCTTION	↑	↑↓	↑														
	EXTENSIONAL VISCOSITY FUNCTION	↑	↑↓	↑														
	SOLIDIFICATION KINETICS	↑	↓	↑														
EXTRUSION																		
	SHEARING HISTORY				Δ													
	EXTRUSION TEMPERATURE					Δ												
	CAPILLARY DIAMETER						Δ											
	CAPILLARY LENGTH							Δ										
	CAPILLARY ENTRANCE ANGLE								Δ									
	POLYMER FLOW RATE									Δ								
	SHEAR RATE						↓			↑								
	SHEAR STRESS	↑	↑↓	↑	↑↓	↓	↓	↑	↑↓	↑								
	DIE SWELL	↑	↑↓	↑	↑↓	↓	↓	↓	↑	↑								
	CHAIN ENTANGLEMENTS	↑	↑↓	↑	↑	↓	↓	↓	?	↑								
QUENCH or SOLVENT REMOVAL																		
	LENGTH OF THE ZONE										Δ							
	TAKE-UP VELOCITY or FORCE											Δ						
HEAT/ /MASS TRANSF. AGENT	FLOW VELOCITY												Δ					
	TEMPERATURE PROFILE													Δ				
	CONCENTRATION PROFILE*														Δ			
	FIBER TEMPERATURE PROFILE	↑↓	?	↑↓	↑↓	↑	↑	↑↓	↑	↑	↑↓	↑↓	↓	↑	↑↓			
	SOLVENT CONTENT PROFILE*	↓	?	↑	?	↓	↑	?	?	?	↓	↓	↓	↑↓	↑			
	FIBER DIAMETER PROFILE	↑↓	↑↓	↑↓	↑	↓	↑	↑↓	↑↓	↑	↑↓	↓	↑↓	↑↓	↑			
	EXTENSIONAL STRESS PROFILE	↑↓	↑↓	↑↓	↑	↓	↓	↑↓	↑↓	↓	↑↓	↑	↑↓	↑↓	↑↓			
	UNRELAXED STRESS PROFILE	↑↓	↑↓	↑↓	↑↓	↓	↓	↑↓	↑↓	↓	↑↓	↑	↑↓	↑↓	↑↓			
	SOLIDIFICATION PROFILE	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑↓	↑↓	↑↓			
COLD DRAWING (PLASTIC DEFORMATION)																		
	DRAW RATIO															Δ		
	RATE OF DRAWING																Δ	
	TEMPERATURE OF DRAWING																	Δ
	NATURAL DRAW RATIO	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↑	↓
	MAXIMUM DRAW RATIO	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↓	↑
	MAXIMUM DRAWING TEMPERATURE	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↓	
	DRAWING TENSION PROFILE	↑	↑↓	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↓

Δ Intentional increase; ↑ Resulting increase; ↓ Resulting decrease; ↑↓ Result depends also on other variables. ? Effect unknown. * Concerns only solution or gel processes.

VIII.2.a Polymer Related Variables

The **Molecular mass function** and its importance have been discussed in many places throughout this book. Its importance from the technological point of view remains the same as from the theoretical one. The full function is best described by the whole curve of the amount of species of different molar mass. In practice it is given mostly by the averages of different kinds and their ratios describing the *distribution of molar masses.* The "shorthand representations" are derivable from the whole curve; on some occasions they are convenient as different polymer properties depend on the averages of different type.

Should all the other independent variables be held constant, then all of the dependent variables would be affected by a change in the molecular mass function. In table VIII.2, such an interdependence is demonstrated. A triangle in the row of an independent variable denotes an intentional increase of this variable, or shift upwards of the entire function with all other independent variables held constant. In the corresponding column, arrows indicate an increase or decrease of value of the dependent variables. A double, up and down, arrows indicates a complicated relationship where the direction of the change may depend on the setting of other variables.

Imperfections of polymer structure are almost equally important as the polymer itself, since they modify the polymer properties. This variable must be classified as independent, although in practice the imperfections are very difficult, often impossible, to control; they *just happen.* Taken from a different side, a change of vendor may mean a change of manufacturing process resulting in a different set of chain distortions, perhaps with less damaging consequences.

Phase composition here means concentrations of the chosen polymer in the chosen solvent. This is undoubtedly an independent variable of high importance, though absent in processes of formation from the melt. This variable affects practically all dependent variables, just as the molecular mass does.

Relaxation and retardation functions depend strongly on the molecular mass and, naturally, on the polymer and its character. Naturally, the relaxation processes are influenced by the presence and quality of solvent. They cannot be changed independently, though often it would be convenient to have such a possibility. Dependence of retardation/relaxation function on applied stresses is stipulated.

Shear and extensional viscosities are equally dependent on molecular mass, solvent (if present), structural perfection, and on other variables located further down on the list.

Solidification kinetics is an inherent property of a polymer, of its molecular mass and other variables. It cannot be changed independently. Imperfections of polymer chain usually slow the kinetics down, however, depending on the nature of the polymer and of the structural distortions, other directions in the changes of kinetics are not out of question.

VIII.2.b Variables in Fiber Extrusion

Shearing history is, to a large extent, a dependent variable since every polymer accumulates some history since its synthesis. Nonetheless, the same variable may be viewed as independent as the accumulated effects of history may be affected by the subsequent shearing and relaxation (temperature effects). The possibilities of modifying the history have been taken as the ground to recognize the history as independent variable, or rather as a variable of qualified independence. It is primarily a matter of chain entanglements but, one may also include here effects of possible shear and/or thermal degradation.

Extrusion temperature is an independent variable of far reaching and strong consequences.

Capillary diameter and capillary length represent two independent variables which may be limited only by technological reasons. The variables have strong effects on other variables, as well as an influence on the phase change kinetics and on the polymer morphology.

The **Capillary entrance angle** represents an independent variable, though preferably it ought to be small in practically all cases.

Polymer flow rate is an independent variable with very strong and far reaching effects on many variables in the process. Those far reaching indirect effects are often underrated. On the other hand, this variable may be the subject of severe technological limitations.

Shear rate depends on the capillary diameter and on the polymer flow rate. This variable is dependent, but it has the smallest number of determinants. Shear rate influences many other variables, mainly those related to rheology.

Shear stress is a typical dependent variable with many independent variables controlling its magnitude.

Die swell results from a number of factors and determines the starting point of the diameter attenuation. Its nature and significance still require research.

Chain entanglements are affected by the shearing history. Repeated consideration of this may appear redundant but it is to reflect the changing nature of the polymer chain morphology. Under the heading of "shearing history" above we understand the state of the polymer as it is coming into the extrusion. Here we consider how the extrusion process changes it, what kind of polymer is going out of the extrusion section, and further, what is entering into the processes of quench zone after relaxation in the die swell.

VIII.2.c Variables in Quench or Solvent Removal

The **length of the quench or coagulation zone** is without any doubt an independent variable from the point of view of hardware. In the technological sense, it is a dependent variable. Depending on the cooling intensity, a filament may be solidified after passing only a fraction of the physical length of the zone.

If such a thing happens, then over the rest of the distance other processes take place, though they should take place in another segment of the line under much better control. Physically the length of the zone may not be shorter than some minimum necessary for cooling. It should not be longer than necessary, as this would be detrimental to the proper process control.

Take-up velocity or force – one of these two is independent, the other is dependent. Which one is which depends on the choice of fiber transport. Roller transport is a constant velocity device and force is whatever results from the velocity, the rheological properties, etc. Pneumatic transport, for example, is essentially a constant force device (provided the filament diameter is constant) and velocity is whatever results from the force and rheology, temperature, etc.

Flow velocity profile regards the velocity of cooling air or of the mass exchange medium. This independent variable "cooperates" with several other independent variables.

Temperature profile regards the temperature of the cooling and/or mass exchange medium. It also has highly cooperative significance, similar to the previous variable.

Concentration profile regards only processes involving solvents and describes the concentration of the mass exchange medium along the filament path.

Fiber temperature profile represents an enormously important variable which cannot be changed independently. There are many independent variables which affect the temperature profile which makes the variable difficult to control positively.

Solvent content profile is valid only for solution or gel processes. It is a result of many independent and dependent variables, similar to the temperature profile.

Fiber diameter profile, like the other variables of the quench zone, is highly dependent on many other dependent variables. The diameter profile itself has strong influence on temperature, solvent content. The fiber diameter profile determines the *time scale* of the process, and further, it determines the residence time of the polymer at any point of the linear distance from the spinnerette.

Extensional stress profile is again highly dependent on many variables and controls other processes, mainly the diameter attenuation profile and phase changes.

Unrelaxed stress profile depends on many variables in a rather complex way, primarily on the level of strain and stress retardation, which themselves depend on other variables. Unrelaxed stress is decisive in acceleration of the crystallization process and in the final fiber morphology.

Solidification profile is equally important in melt as it is in solution processes. It determines the melting profile of a crystalline fiber. In solution processes it determines additionally the structural uniformity along the fiber radius.

VIII.2.d Variables of Cold Drawing

The **Draw ratio**, or as otherwise called plastic deformation, is the main variable responsible for imparting a structural and property orientation along the fiber axis. It is an independent variable within technological limits, provided the drawing is done with positive (roller) transport. When fibers are transported by pneumatic jets, that is with *quasi constant force*, the variable is not exactly independent; the drag force depends on the fiber diameter and on the resultant fiber velocity. In effect, it is constant only with a very stable process.

Rate of drawing may be an independent variable if the drawing process is executed separately from the previous stages of fiber formation. In cases where the drawing operation is performed in-line with the entire process, the rate of drawing may need to be subordinated to the take-up velocity and draw ratio. In the case of pneumatic transport it becomes vulnerable to the changes resulting from the potential variations of draw ratio.

Temperature of drawing is similarly an independent variable with qualification. The process of plastic deformation is exothermic, and this introduces certain dependence on the control of drawing temperature. Any instability of draw ratio and/or drawing rate is bound to be reflected in the amount and rate of heat generation. The variable heat generation, in turn, will interfere with the temperature control system.

Natural draw ratio depends on the structural features of the undrawn fibers, on total crystallinity, and on a "preorientation" which often may be present. The dependences go all the way back to the molecular mass of the polymer.

Maximum draw ratio has qualitatively similar dependencies as natural draw ratio but the quantitative influence of different factors is different.

Maximum drawing temperature (before the necking disappears) depends on the amount and the type of crystallinity in the undrawn fibers, including melting temperature of the crystals. As the drawing progresses, the maximum drawing temperature usually increases.

Drawing tension profile pertains primarily to cases of multistage drawing. In a single stage drawing the drawing tension is more or less constant.

VIII.3 Process Analyses

Analyses of technological processes are usually performed for one or more of the following three reasons:

- Control of raw materials for agreement with specifications and/or suitability for the process.
- Control of the proper functioning of the process.
- Control of product properties and their agreement with specifications.

Such an analytical routine should be introduced already during process development. This facilitates process start-up and provides the best tools for so called *trouble shooting.* It is certainly much better to have the tools, and an "exemplary" data bank, prepared in time, before any bad events begin to be pressing.

Analyses of fiber formation processes ought to be divided in agreement with the technology requirements, that is, according to the four groups of technological variables.

All of the analytical work on polymers is related to the following three areas:

- Physico-chemical characterization of polymers: molecular mass, structural purity, as well as solvents and solubility if needed.
- Rheological analysis, mainly in oscillatory mode, in some cases reinforced by a rotational mode, and/or capillary measurements.
- Crystallization kinetics and thermal properties.

The depth of these analyses should depend on the type and character of the polymer used. Some polymers may require more detailed rheological analysis, which is *per se* very sensitive and may serve as an indicator that something is different in the chain structure. Other polymers, including some polycondensation products, may require more physico-chemical determinations, while still others may need to be analyzed for cross linked material.

Economic sensitivity obviously calls for a minimum of analytical work. On the other hand, poor results in manufacturing may cost substantially more than the systematic analyses would. Capabilities of more detailed determinations should be accessible in case more serious problems should develop.

The segment of extrusion represents no problems as far as analyses are concerned. The spinnerette design is fixed for a given process, extrusion conditions are usually controlled and recorded automatically. Metering pumps are normally reliable, with automatically controlled velocities and recorded polymer pressure.

The only variable of concern may be the die swell, and how constant it is for a given process. The potential die swell variability may be also connected with changes of chain entanglements. None of the two variables may be controlled independently, but any change of them would indicate changes of polymer, either its chemical nature or its physical state. Warnings of such changes and their magnitude should be obtained from the polymer characterization.

Control of the quench or coagulation zone represents an entirely different, infinitely more complex task. The independent variables may be controlled fairly easily. They are either constant for the process, like the physical length of the quench (coagulation zone), or readily controlled, like flow, distribution and temperature of the heat and/or mass transfer agents. The dependent variables may represent serious difficulties and therefore characterization of the quench zone processes is treated in a separate section.

In a cold drawing operation, the independent variables must be qualified, as elaborated above. Assuming a positive transport system and independently controlled draw ratio and drawing rate, the temperature of drawing may be controlled only indirectly through the heating/cooling device. Direct control of the filament temperature would require infrared devices, and so far this is not done on a standard, operational basis.

The dependent variables of the drawing zone are immaterial in a well established process, provided that there are sufficient *safety margins, e.g.* for the maximum draw ratio and maximum drawing temperature.

VIII.4 Description of Quench and Coagulation

The group of dependent variables in quench and/or coagulation processes forms a closed circle of *causes and effects*. All of the dependent variables have nonlinear relationships and are mutually interdependent. The relatively large number of them, five or six, places the system into danger of the *butterfly effect*. It is not exactly to a degree comparable to the famous butterfly in China triggering a hurricane in the Atlantic, but it is sufficient to affect the stability of a process to a degree clearly detectable in the quality of the manufactured product. An attempt of a "visual" presentation of the complexity of the interdependencies is presented in figure VIII.1.

It is necessary to stress that all the variables given in figure VIII.1 represent nonlinear functions of either distance or time lapsed from the spinnerette, or rather from the maximum of die swell. For the process of formation from a melt, Nusselt number is used, which *per se* is not a variable. Nevertheless, it was used here to stress the complexity of the influences on temperature. A similar situation exists in the wet process, where the heat exchange is not so dramatically affected unless there is a large difference between the temperature of extrusion and the temperature of the coagulation bath. In the case of dry processes the influence of the concentration function on temperature is indicated. This is meant to stress the influence of rapidly evaporating solvent on temperature through the heat of evaporation. The obvious influence of temperature on the *modus* of crystallization is omitted to avoid more complications on the already busy diagrams.

The unusual complexity of the dependencies represents a very good reason why it is so difficult to develop a satisfactory quantitative description of the processes. At the same time, the diagrams of figure VIII.1 explain why an consideration of a part of the problem offers little hope for real success – to make progress all the necessary influences must be considered. Also, particular care should be taken with the simplifications of any mathematical solutions. One has to bear in mind that we speak of products with diameters in the range of microns and processes where every degree of temperature is meaningful. All this causes the demand for a high degree of accuracy and a very low tolerance for errors.

To describe a fiber formation process, a certain number of experimental characterizations are unavoidable. The relationship between the unrelaxed stress and temperature for the onset of the process of crystallization is described in section IV.5. However, the diameter attenuation and unrelaxed stress may be pre-

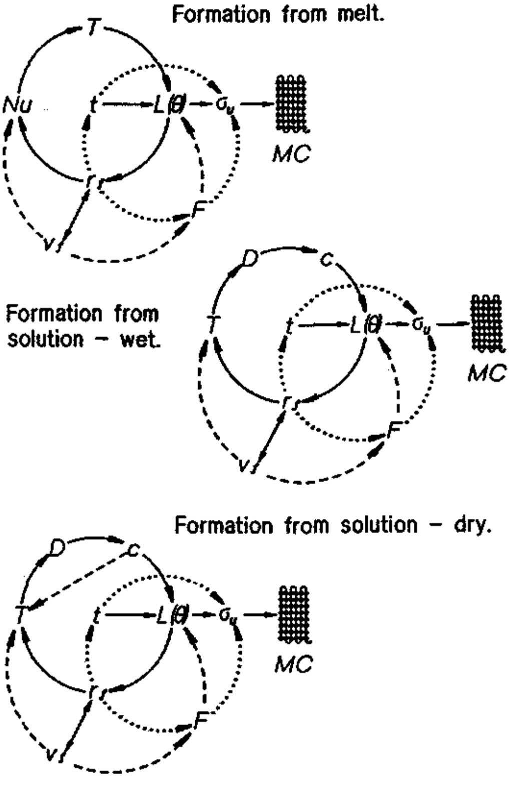

Figure VIII.1: *Schematic representation of the interdependencies of variables in quench and coagulation zone. Symbols: T is filament temperature, Nu is Nusselt number, t is time, r_f is radius of filament, v_f is velocity of filament, F is extensional force, $L(\theta)$ is creep retardation function, σ_u is unrelaxed stress, D is diffusivity, c is concentration; all the values represent functions versus distance from spinnerette or time.*

dicted with some qualifications, and the initiation of crystallization can be predicted in a way similar to figures IV.28 through IV.30. The process of crystal growth is still unpredictable. For this reason laboratory determination of polymer crystallization and of *crystallization history* (CH) is highly recommended. The crystallization profile is necessary to calculate the filament temperature profile with a sufficient accuracy. In reverse, the temperature profile must also be determined to define the "location" of the crystallization profile.

From experience, as reported in the previous chapters, we know that the most accurate description of diameter attenuation is obtainable when the process is considered in terms of creep relaxation. On the other hand, it has been demonstrated that the creep retardation function is not universally constant: it depends also on the magnitude of the applied initial stress. These relationships are known to allow neither an *a priori* prediction of the retardation function, nor limits of its validity. In effect, the function must be determined experimentally and it may be used only for cases where the initial stresses do not deviate significantly. The specific conditions of any formation process, particularly its velocity, are difficult to simulate in any laboratory instrumental characterization. All this leads to the necessity of experimental determination of filament diameter and/or velocity profile together with the temperature profile. Shortly, a whole characterization of the whole quench zone is necessary to describe the process.

In the case of wet formation from solution, the concentration profile may be calculated with fair accuracy. In dry formation, the sensitivity of the process to the temperature profile makes it rather necessary to determine experimentally both the temperature and the concentration profiles.

Since different events are taking place simultaneously in the discussed segment of the process, the evaluation of many of the experimentally gathered data should be performed simultaneously, in one computational run. This means that, for example, the solution of the differential equations for the heat transfer and for the diffusion of solvent should be done in parallel, step by step; the results from each of the strings of calculations should be fed into the other strings as the computation progresses. Parameters, which in many publications are taken as constants, like density, heat conductivity, and others, should be step by step corrected for actual temperature, concentration, etc. All of the calculations here are based on differential equations, and error propagation in such cases is exceptionally large. Results of such calculations are given in figure IV.4.

To obtain reasonably accurate results, the number of points calculated over radius should not be smaller than eight, but more than sixteen points might call for accuracies of experimental data which are unattainable. Many methods of solution of differential equations require the number of points in the axial direction to match the number of points in the radial direction, and if so, this is an important point.

Another important point to be made is that the experimental data need to be of high precision, naturally, with points taken as densely as practical. As the number of points calculated in the axial direction will always be larger than the number of experimental points, an interpolation technique must be used. It is advisable not to smooth the data, or many important features may be lost. One needs an open mind about unexpected events. A case in point may be seen in figure VIII.2, which presents extension rate plotted against distance from spinnerette, filament temperature and time.

A closer look at figure VIII.2 shows that the extension rate goes initially through a maximum, which has been denied by some authors. Yet all the examples quoted here show this behavior, as do all of the many cases studied, irrespectively of the polymer. Certain segments of the curves are drawn in thick lines to indicate where crystallization was taking place. From these it is evident that crystallization starts in the vicinity of the first minimum of the curves. After the first peak in the curves follow two or three peaks, much steeper and larger then the first one. The process of crystallization coincides with the first large peak, sometimes the whole peak, sometimes one half of it, or so. The next large peak indicates onset of neck drawing. Presence of such peak indicates too long a quench zone.

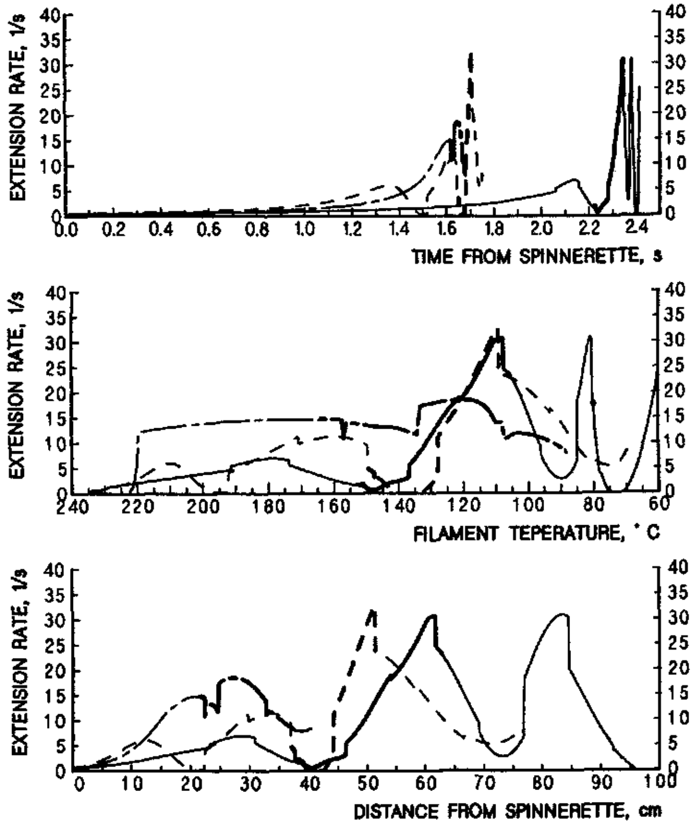

Figure VIII.2: *Dependence of extension rate on time, temperature, and distance from spinnerette. Different line patterns represent processes with different effective lengths of quench zones. Heavy line segment indicates crystallization.*

It is important to note that in the area where crystallization takes place and in the area of necking, the curves are bumpy. Such bumps are always present in the area of crystallization and indicate some instabilities. In the area of necking the instabilities appear often in fast "one step" processes without separation into formation and drawing zones. Such instabilities indicate that the drawing is out of control. Smoothing out of the input data might remove the bumps and show the process as fully stable when it really is not.

Calculations of the forces acting on filaments cannot be performed in the same group as above; a second group must be formed. Force of gravity, inertia, fluid dynamic drag force, force of momentum all must be integrated from the point of fiber take-up upwards to the spinnerette. These calculations must go then in the opposite direction as those of the first group. The outcome of such force calculations is presented in figure IV.3.

After the second group of calculations has been done, one may use the results on the available force and the results obtained in the first group of calculations to obtain the creep retardation function, as given in figure IV.23.

Subsequently, calculations may be performed involving various correlations, such as heat transfer coefficient (provided the cooling medium data have been collected.

It is quite clear that such a characterization represents a fairly large task, and as such cannot be performed routinely. Such work, however, should be performed during development of a process and from time to time in manufacturing to prevent the "drifting" of a process.

VIII.5 Prediction of Quench and Coagulation

It is the goal of every technology to predict the process, to be able to calculate everything *a priori*, and use experiment just for the confirmation of the accuracy of calculations. The technology of fiber formation, despite its age and commercial importance, clearly is not developed to this point yet.

The main points which currently are developed insufficiently for full predictability are

- Calculation, or recalculation, of the creep retardation functions *a priori*, theoretically.
- Description of the kinetics of polymer crystallization, particularly crystallization under strain.

It is possible to perform a number of process characterizations, as described above, during the development stage of a process. Correlations may be obtained for a polymer and a process, and based on this it may be possible to construct systems of calculations which would predict, *e.g.* operating conditions for machines to offset small variations of raw material, or similar. Investment of time and effort in such partial, semiempirical correlations is highly recommended as worthwhile and economically highly justified. Naturally, such correlations must be done with full respect for the process complexity and with the proper separation of variables. Otherwise, the outcome may be misleading.

As for knowledge of the missing links, this is a task for further research in rheology to discover exactly what affects the creep retardation functions and how they are affected. Such information represents a necessary minimum for full predictability of the rheological behavior of polymer, filament attenuation and interaction with the process of crystallization initiation and crystal growth.

Another area needing effort involves cooperation between kinetics of crystal growth in conjunction with rheology. Special attention to the morphology of polymer melts would be very helpful. Morphology of the melts is of high importance to rheology. Rheology provides an indirect measure of basically unknown conformational states, and those conformations are most likely the quantities contributing to the crystal growth. The "interdisciplinary" character of the task adds to the difficulty.

VIII.6 References

1. Z. K. Walczak: *Formation of Synthetic Fibers*, Gordon and Breach, London - New York, 1977, Chapter 6.