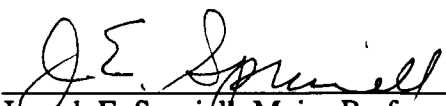
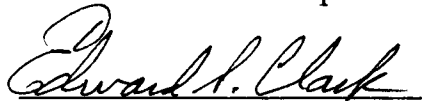


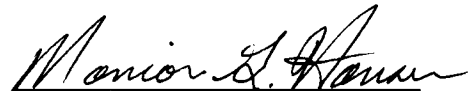
To the Graduate Council:

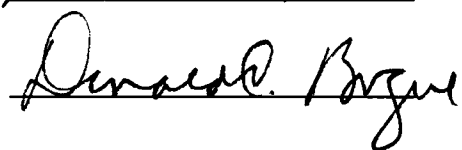
I am submitting herewith a dissertation written by Rajen M. Patel entitled "Modeling of Fiber Spinning and Crystallization Kinetics During Polymer Processing." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Polymer Engineering.


Joseph E. Spruiell, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:


Vice Provost
and Dean of The Graduate School

MODELING OF FIBER SPINNING AND CRYSTALLIZATION KINETICS
DURING POLYMER PROCESSING

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Rajen M. Patel

August 1991

ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to his advisor, Professor Joseph E. Spruiell, for his guidance, suggestions, and patience during the course of this work.

The author also thanks his committee, Professors J. E. Spruiell, D. C. Bogue, M. G. Hansen, and E. S. Clark, for their effort in making this work possible. The author wishes to extend special thanks to his former advisor, Professor Donald C. Bogue, for many helpful discussions during his stay at the University of Tennessee.

The author thanks the Allied Fibers and Dow Chemicals for the financial support provided throughout this work. The author also wishes to extend special thanks to Dr. Ronnie Moore of Allied Fibers for helpful discussions throughout this work.

The author appreciates the many discussions with his fellow students and friends. The author wishes to extend special thanks to Dr. Young D. Lee, Mr. Vinod Shah and Mr. Nejib Hajji for their help during the course of the present work. The author appreciates the technical help provided by the electronics shop and machine shop.

Finally, the author wishes to express his deepest gratitude to his family and his wife for their support and love.

ABSTRACT

A multitude of process and resin variables affect the melt spinning process. Hence, a mathematical model of the process is quite valuable for developing an understanding of the process and for predicting spinline behavior under a variety of process conditions. It was the basic purpose of the present research to develop an improved process model for melt spinning of fibers with a better understanding of polymer rheology and polymer physics underlying the spinline dynamics and structure development.

The spinline model developed by Zieminski using the CSMP package on the IBM mainframe was improved, simplified and implemented on the IBM PC. The development and description of the Newtonian spinline model is given in Chapter 4. The inversion procedure used by Bheda was improved, simplified and implemented on the IBM PC. An improved inversion procedure is described and is shown to give better results for the computed apparent elongational viscosity data of the nylon 6 resins and heat transfer coefficient data. The model predictions compared well with the experimental on-spinline measurements on two nylon 6 resins carried out by Bheda. The results show that the model describes the major features of the melt spinning process.

An analysis of available methods of dealing with polymer crystallization for process modeling is presented. Problems encountered in using isothermal data to predict nonisothermal results are discussed and illustrated using experimental data for two nylon 6 resins. A half-time analysis is used to evaluate and extrapolate the isothermal crystallization rates. It is concluded that none of the available models are entirely satisfactory for computing nonisothermal crystallization from isothermal data, though the

Nakamura model is shown to be more satisfactory for process modeling than other models discussed in the literature. A nonlinear regression method is presented for directly fitting nonisothermal crystallinity data using the Nakamura model to obtain crystallization rate equation parameters. Two empirical methods for including amorphous orientation effects are also considered and evaluated by comparing predicted results to online experimental data for melt spinning of nylon 6.

The basic rheological data on various nylon 6 resins supplied by Allied Fibers were measured using a cone-and-plate rheometer and a capillary rheometer. The melt spinning studies of those resins were carried out using on-spline measurements. The melt spinning measurements were used to compute spinline elongational viscosity data of various Allied nylon 6 resins and heat transfer coefficient correlation data using the improved inversion procedure. The applications of the Newtonian spinline model in understanding the role of various process and resin variables in determining spinline behavior are described.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION	1
2. BACKGROUND	5
2.1 Dynamics of Spinning Process	5
2.2 Melt Rheology and Constitutive Equation	8
2.3 Energy Balance	18
2.4 Crystallization Kinetics	20
2.5 Orientation and Birefringence in Flowing Melts	41
2.6 Structure Development in Fiber Spinning	42
2.7 Mathematical Modeling of Fiber-spinning	45
3. MATERIALS AND EXPERIMENTAL PROCEDURE	53
3.1 Materials	53
3.2 Experimental Procedures	55
4. DEVELOPMENT AND DESCRIPTION OF MELT SPINNING MODELING PROGRAM.....	64
5. ANALYSIS OF CN 9984 AND BHS SPINLINE DATA	77
5.1 Inversion Procedure and Evaluation of Elongational Viscosity and Heat Transfer Coefficient	78
5.2 Mathematical Modeling	85
6. CRYSTALLIZATION KINETICS DURING PROCESSING -- ANALYSIS AVAILABLE APPROACHES	104
6.1 Quiescent Isothermal Kinetics	104
6.2 Quiescent Nonisothermal Kinetics	114
6.3 Orientation Effects in Melt Spinning	133
7. BASIC RHEOLOGICAL AND MELT SPINNING STUDIES OF BHS, LSB MBM RESINS	137

7.1 Basic Rheological Measurements	137
7.2 Melt Spinning of Allied BHS, LSB and MBM Resins	145
8. APPLICATIONS OF THE NEWTONIAN SPINLINE MODEL	160
9. CONCLUSIONS	194
LIST OF REFERENCES	198
APPENDIX	206
VITA	212

LIST OF TABLES

TABLE	PAGE
1. The GPC data of various Allied nylon 6 resins.	54
2. Tabulation of initial rheological forces tried and corresponding predicted take-up velocities.	73
3. Comparison of predicted take-up force with the experimentally measured values for CN 9984 resin.	99
4. Comparison of predicted take-up force with the experimentally measured values for BHS resin.	100
5. Tabulation of half-times and Avrami indices at various crystallization temperatures for BHS resin.	110
6. Tabulation of half-times and Avrami indices at various crystallization temperatures for MBM-I resin.	111
7. Values of the Ozawa exponent at various temperatures for BHS and MBM-I resins.	120
8. Tabulation of K_0 values for various C_3 values for BHS at different cooling rates obtained using Equation [6.2.1].	129
9. Basic rheological data of BHS resin.	138
10. Basic rheological data of MBM-I resin.	139
11. Basic rheological data of MBM-II resin.	140
12. Basic rheological data of MBM-III resin.	141
13. Basic rheological data of LSB resin.	142
14. Basic rheological data of washed MBM-II resin.	143
15. Summary of experimental processing conditions.	147
16. Summary of process conditions chosen for simulation.	161

LIST OF FIGURES

FIGURE	PAGE
2.1. Schematic illustration of the concept of a "continuous cooling transformation curve" showing the anticipated effect of stress in shifting such curves.	40
3.1. Schematic diagram of the spinning equipment.	56
4.1. Summary of the working relationships of the improved fiber spinning model.	65
5.1. Schematic diagram of the inversion procedure for computing the apparent elongational viscosity and heat transfer coefficient from experimental on-line measurements of spinline diameter, temperature and tension.	80
5.2. Calculated apparent elongational viscosity using improved inversion procedure and zero-shear viscosity for BHS resin at two throughput rates.	82
5.3. Calculated heat transfer coefficient correlation using improved inversion procedure for BHS and CN 9984 resins each for two throughput rates. ...	84
5.4. Comparison of the model predictions with the on-line diameter measurements for BHS resin melt spun with a mass throughput of 2.993 g/min.	88
5.5. Comparison of the model predictions with the on-line diameter measurements for BHS resin melt spun with a mass throughput of 5.069 g/min.	89
5.6. Comparison of the model predictions with the on-line temperature measurements for BHS resin melt spun with a mass throughput of 2.993 g/min.	90
5.7. Comparison of the model predictions with the on-line temperature measurements for BHS resin melt spun with a mass throughput of 5.069 g/min.	91
5.8. Comparison of the model predictions with the on-line birefringence measurements for BHS resin melt spun with a mass throughput of 2.993 g/min.	92
5.9. Comparison of the model predictions with the on-line birefringence measurements for BHS resin melt spun with a mass throughput of 5.069g/min.	93
5.10. Comparison of the model predictions with the on-line diameter measurements for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.	94

FIGURE	PAGE
5.11. Comparison of the model predictions with the on-line temperature measurements for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.	95
5.12. Comparison of the model predictions with the on-line birefringence measurements for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.	96
5.13. Computed crystallinity profiles for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.	97
5.14. Effects of mass throughput rate and the resin molecular weight on the simulated temperature profiles at a take-up velocity of 7000 m/min.	98
6.1. Isothermal crystallization kinetics data for BHS at various crystallization temperatures.	105
6.2. Isothermal crystallization kinetics data for MBM at various crystallization temperatures.	106
6.3. Avrami analysis of BHS isothermal crystallinity data.	107
6.4. Avrami analysis of MBM isothermal crystallinity data.	108
6.5. Plot of $\ln(1/t_{1/2}) + U^*/R(T-T_\infty)$ versus $1/(T\Delta T f)$ for BHS and MBM isothermal kinetics data.	112
6.6. Plot of extrapolated half-times as a function of temperature. (—) is the data of BHS; (----) is the data of MBM; and (— —) is nylon 6 half-time data from literature.	113
6.7. Nonisothermal crystallization data of BHS resin.	115
6.8. Nonisothermal crystallization data of MBM resin.	116
6.9. Ozawa analysis of BHS nonisothermal crystallization data.	118
6.10. Ozawa analysis of MBM nonisothermal crystallization data.	119
6.11. Comparison of experimental and predicted nonisothermal crystallinity data of BHS using the integral Kamal model at different cooling rates. Solid lines are predictions using $T_0=250^\circ\text{C}$ and dashed lines are predictions using $T_0=210^\circ\text{C}$	121

FIGURE	PAGE
6.12. Comparison of experimental and predicted nonisothermal crystallinity data of BHS using the integral Nakamura model at different cooling rates. Solid lines are predictions using $T_0=250\text{ }^{\circ}\text{C}$ and dashed lines are predictions using $T_0=210\text{ }^{\circ}\text{C}$	122
6.13. Comparison of experimental and predicted nonisothermal crystallinity data of BHS using the differential form of the Nakamura model at different cooling rates.	125
6.14. Comparison of experimental and predicted nonisothermal crystallinity data of MBM using the differential form of the Nakamura model at different cooling rates.	126
6.15. Non-linear regression fitting of the nonisothermal crystallization data of BHS using the differential form of the Nakamura model.	131
6.16. Non-linear regression fitting of the nonisothermal crystallization data of MBM using the differential form of the Nakamura model.	132
6.17. Comparison of the spinline model predictions using measured quiescent kinetics data with the on-line birefringence measurements for BHS resin melt spun with a mass throughput of 2.993 m/min.	135
7.1. Shear viscosity data for BHS and MBM-I resins at various temperatures.	144
7.2. The diameter profiles for MBM-II and MBM-III resins spun at various take-up velocities.	148
7.3. The temperature profiles for MBM-II and MBM-III resins spun at the same mass throughput rate.	150
7.4. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for MBM-II and MBM-III resins.	152
7.5. The diameter profiles of BHS and LSB resins spun at various take-up velocities.	153
7.6. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for BHS and LSB resins.	155
7.7. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for various nylon 6 resins.	156
7.8. The plot of calculated heat transfer coefficient for various resins.	158
8.1. The predicted diameter profiles for circular filament spun at 2000 m/min at two throughput rates.	162

FIGURE	PAGE
8.2. The predicted temperature profiles for circular filament spun at 2000 m/min at two throughput rates.	163
8.3. The predicted stress profiles for circular filament spun at 2000 m/min at two throughput rates.	164
8.4. The predicted amorphous birefringence profiles for circular filament spun at 2000 m/min at two throughput rates.	165
8.5. The predicted amorphous and total birefringence profiles for circular filament spun at 2000 m/min at two throughput rates.	166
8.6. The predicted diameter profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.	170
8.7. The predicted temperature profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.	171
8.8. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.	172
8.9. The predicted total birefringence profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.	173
8.10. The predicted crystallinity profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.	174
8.11. The predicted diameter profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.	176
8.12. The predicted temperature profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.	177
8.13. The predicted stress profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.	178
8.14. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.	179
8.15. The predicted diameter profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for MBM and BHS resins. .	180

FIGURE	PAGE
8.16. The predicted temperature profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for MBM and BHS resins.	181
8.17. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for MBM and BHS resins.	182
8.18. The predicted diameter profiles for circular and triangular filaments at throughput rate of 5 g/min and at take-up velocity of 2000 m/min.	185
8.19. The predicted temperature profiles for circular and triangular filaments at throughput rate of 5 g/min and at take-up velocity of 2000 m/min.	186
8.20. The predicted amorphous birefringence profiles for circular and triangular filaments at throughput rate of 5 g/min and at take-up velocity of 2000 m/min.	187
8.21. The predicted temperature profiles for circular and triangular shaped spinneret at the take-up velocity of 6000 m/min.	188
8.22. The predicted diameter profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for two different quench conditions.	191
8.23. The predicted temperature profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for two different quench conditions.	192
8.24. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for two different quench conditions.	193

NOMENCLATURE

z = Distance from spinneret.

W = Mass throughput rate.

V = Filament velocity.

D = Filament diameter.

ρ = Filament density.

ρ_a = Density of air.

σ = Surface tension at polymer melt/air interface.

σ_f = Shear stress at fiber-air interface due to aerodynamic drag.

C_d = Drag coefficient.

g = Acceleration due to gravity.

Re = Air Reynolds number.

σ_{11} = Axial spinline stress.

T_{ij} = Deviatoric stress tensor.

δ_{ij} = Kroneker delta.

μ = Newtonian viscosity.

γ = Shear rate, nylon - 6 hexagonal modification.

η_e = Uniaxial elongational viscosity.

η_{eapp} = Apparent elongational (spinline) viscosity.

E = Elongation rate.

A = Activation energy.

R = Universal gas constant.

G = Shear modulus.

τ = Relaxation time.

N_1 = First normal stress difference.

N_2 = Second normal stress difference.

π_d = Second invariant of the deformation rate tensor.

a = Thinning parameter.

C_{ij}^{-1} = Finger strain tensor.

D/Dt = Material time derivative.

$\delta/\delta t$ = Oldroyd contravariant convected time derivative.

h = Heat transfer coefficient.

T = Filament temperature.

T_a = Ambient temperature.

ΔH_f = Heat of fusion.

X = Crystalline fraction.

C_p = Heat capacity of polymer melt.

μ_{air} = Viscosity of air.

U_c = Cross-air flow velocity.

k_{air} = Thermal conductivity of air.

G = Linear growth rate of spherulites.

T_m^0 = Equilibrium melting point.

k = Isothermal Avrami rate constant.

$t_{1/2}$ = Crystallization half times.

n = Avrami index.

f = Correction factor for Δh_f .

U^* = Activation energy for segmental jump rate.

$\mu(\tau)$ = Rate of sporadic nucleation at time τ .

R = Cooling (or heating) rate.

X_∞ = Crystallinity at the termination, maximum achievable crystallinity.

$A(T)$ = Stress-induced crystallization parameter in Ziabicki formulation.

C = Stress-induced crystallization parameter in extended half-time analysis.

λ = Extension ratio.

C_{op} = Stress-optical coefficient.

α = Polarizability of the random link in Kuhn's model.

f_a = Average amorphous orientation factor, Crystalline a-axis orientation factor.

f_c = Crystalline c-axis orientation factor.

η_0 = Zero-shear viscosity.

Δ_a = Intrinsic amorphous birefringence.

Δ_c = Intrinsic crystalline birefringence.

CHAPTER 1

INTRODUCTION

Melt spinning is by far the most common method for producing continuous fine denier filaments from organic polymeric materials and inorganic glasses. The process of melt spinning apparently dates back to an 1845 English patent by R. A. Brooman (1) who conceived the basic idea as a method of preparing filaments from gutta percha. The first commercially successful application was based on the research of Carothers (2,3) which led in 1939 to a process for production of nylon-66 filament by E. I. duPont de Nemours. Due to inherently low production costs the process has since found an ever increasing number of applications and significant effort has been expended in the last 25 years to better understand the dynamics and the structure development during the fiber spinning process.

Although seemingly simple, the melt spinning process contains many variables which interact with one another and make a complete understanding of it quite difficult. The primary independent process variables include 1) the mass flow rate of the polymer melt, 2) the take-up velocity of the wound up filaments, 3) the extrusion temperature, 4) the spinneret orifice shape and dimensions, 5) the spinline length, and 6) the cooling condition along the spinline. In addition, a multitude of resin characteristics interact with the process variables to influence the processing-structure-properties relationships of the spun filaments. The resin characteristics which play a significant role in determining these relationships are chemical nature of the molecule and molecular weight and its distribution.

Because of the large number of interacting variables that affect the melt spinning

process, a mathematical model of the process is quite valuable for developing an understanding of the process. Although there have been a number of previous attempts to model the melt spinning process, most have omitted crystallization phenomena due to the difficulties of treating nonisothermal crystallization and the effects of molecular orientation (4-12). The time dependent change in degree of crystallinity affects the heat transfer, on-line elongational viscosity and, consequently, the kinematics and dynamics of spinning (13-18). The omission of crystallization phenomena from the model also made it impossible to use the earlier models to help understand how the final structure and properties of melt spun filaments are developed. This is particularly important for melt spinning of polyolefins which always will crystallize on the spinline. Even slowly crystallizing polymers such as nylons and PET will crystallize in the spinline at sufficiently high spinning speeds. As a part of the ongoing fiber spinning research program at the university of Tennessee, Zieminski and Spruiell (13,14) developed a mathematical model to describe the melt spinning of crystallizable polymers. The model included the effects of acceleration, gravity and air friction on the kinematics of the process; temperature and molecular orientation on the crystallization kinetics of the polymer; and temperature, molecular weight and crystallinity on the elongational viscosity of the material. As in any model of a physical system, some assumptions must be made in order to develop a usable set of equations. The set of assumptions stated by Zieminski and Spruiell (13) leads to a system of first order ordinary differential equations with crystallization kinetics equation being an integro-differential equation. Zieminski and several subsequent researchers at the University of Tennessee used the CSMP (Continuous System Modelling Program) utility package on the IBM mainframe computer available through the University of Tennessee Computer Center to solve the system of differential equations. The model assumed the Newtonian constitutive equation to

describe the rheological response of the polymer in the spinline. Under this assumption, the elongational viscosity of the melt is taken to be dependent only on temperature.

It is the basic purpose of the present research to examine various aspects of the spinline model developed by Zieminski with the aim of providing an improved model and a better understanding of the polymer physics underlying the model. The first aspect of the research is to improve upon and modify the spinline model developed by Zieminski which is based on the Newtonian constitutive assumption. The second aspect of the research is to include a "best possible" description of crystallization kinetics that includes the effects of non-isothermal behavior and stress-induced crystallization to describe spinline crystallization.

The spinline model developed by Zieminski assuming Newtonian behavior is improved upon, simplified and implemented on an IBM PC. This Newtonian spinline model requires elongational viscosity data as a function of temperature and heat transfer coefficient data, both to be obtained from an inversion procedure as described by George and Deeg (19) and subsequently implemented by Bheda (17) using the CSMP package on the IBM mainframe. The inversion procedure used by Bheda has also been improved upon and implemented on the IBM PC. The improved inversion procedure is described in chapter 4. The results of the inversion procedure and the spinline model comparison with on-line measurements are discussed in chapters 4 and 5.

The crystallization kinetics required by the model is examined with the goal of providing the best possible description that includes the effects of non-isothermal behavior and stress-induced crystallization. The starting point is an analysis of the quiescent isothermal and non-isothermal kinetics experiments as done by Zhou (20). Since isothermal kinetics data can be obtained only in a narrow temperature range, the Avrami rate constant (or half-time) needs to be extrapolated to lower temperatures. The

measured half-times are described and extrapolated using the Hoffman-Lauritzen theory (called half-time analysis). The Avrami rate constant as a function of temperature can be obtained easily from the extrapolated half-times and can be used to predict nonisothermal crystallization data. Theories for predicting nonisothermal crystallization from isothermal data are reviewed and evaluated in terms of their potential for use in process modeling using nylon 6 quiescent isothermal and nonisothermal and, spinline (stress-induced) crystallization data. A procedure to fit non-isothermal quiescent crystallization data obtained at various cooling rates directly using non-linear regression based on the Marquart algorithm is described to extract the relevant model parameters. This exercise is of practical importance in that it should give improved predictions of quiescent non-isothermal data at high cooling rates, allowing the data to be compared with stress-induced kinetics results obtained in fiber spinning. Various empirical models for including orientation effects in the melt spinning model are examined by comparing model predictions with on-line measurements.

It is also a purpose of the present research to examine various nylon 6 resins provided by Allied Fibers in terms of their rheological, crystallization and melt spinning characteristics. The basic rheological data on the nylon 6 resins were obtained by using a cone-and-plate rheometer and a capillary rheometer. The isothermal and nonisothermal crystallization data of the nylon 6 resins were obtained using a Perkin-Elmer Differential Scanning Calorimeter. The crystallization data were analyzed using appropriate theories of isothermal and nonisothermal crystallization. The apparent spinline elongational viscosity data of the nylon 6 resins and the heat transfer coefficient correlation were obtained from melt spinning of the resins using the improved inversion procedure. These resin characteristics were used in the melt spinning model to predict the spinline behavior of Allied melt spinning processes.

CHAPTER 2

BACKGROUND

The three major processes of man-made fiber formation are melt-spinning, dry spinning and wet spinning (21). Among the three processes the simplest conceptually and hence the most amenable to mathematical simulation is melt-spinning. It is governed by heat transfer and extensional deformation without involving the added complexities of chemical reaction and mass transfer. The primary limitation of the method is due to the fiber forming material which must be fusible and yield thermally stable, spinnable melts. In a typical melt spinning process, molten polymer is extruded through a capillary die; it is then drawn in the molten and/or solid state to impart orientation, strength and tenacity to the fiber. Because of the economic importance of this method, significant effort has been expended in the last 25 years to better understand the dynamics and the structure development during the fiber spinning process.

2.1 Dynamics of Spinning Process

The over-all force balance for fiber spinning can be written as follows (21):

$$F_{rheo} = F_0 + F_{inert} + F_{drag} - F_{grav} - F_{surf} \quad [2.1.1]$$

where: F_{rheo} is the rheological force in the fiber, F_0 is the rheological force at the beginning of the spinline, F_{inert} is the inertial force as the fiber is accelerated, F_{drag} is the drag force caused by the fiber moving through a stationary fluid, F_{grav} is the gravitational force on the fiber, F_{surf} is the surface tension force at the fiber-air interface

and is generally considered negligible compared to the magnitude of the other force components. These forces may be expressed as (21):

$$F_{\text{inert}} = W(V - V_0)$$

$$F_{\text{drag}} = \int_0^z \pi D \sigma_f dz$$

[2.1.2]

$$F_{\text{grav}} = \int_0^z \rho g \left(\frac{\pi D^2}{4} \right) dz$$

$$F_{\text{surf}} = \int_0^z \frac{\pi \sigma}{2} (D_0 - D) dz$$

where D_0 and V_0 are the die diameter and average velocity in the die, respectively. σ_f is the shear stress at fiber-air interface due to aerodynamic drag and σ is the surface tension of polymer melt with respect to air. W is the mass throughput rate, related to other variables through the equation of continuity as $W = \rho A V$ which for a cylindrically shaped filament becomes

$$W = \rho \pi (D/2)^2 V \quad [2.1.3]$$

Neglecting radial variations and the force due to surface tension, the gradient of axial tension along the spinline can be written using [2.1.1] and [2.1.2] as,

$$dF_{\text{rheo}}/dz = W dV/dz + 1/2 \rho_a C_d V^2 \pi D - W g/V \quad [2.1.4]$$

Where D, V and g are filament diameter, filament velocity and the gravitational

acceleration constant, respectively. In the above equation, spinning into a stationary ambient air is assumed. C_d is the drag coefficient and is defined using the equation for the shear stress at fiber-air interface due to aerodynamic drag $\sigma_f = 1/2 \rho_a V^2 C_d$. The differential force balance equation can also be arrived at starting from equations of motion in cylindrical coordinates (22).

The rheological force in the spinline is related to the axial spinline stress σ_{11} (or σ_{zz}) as

$$\sigma_{11} = F_{\text{rheo}}/\pi(D/2)^2 \quad [2.1.5]$$

One of the principal unknowns in the force balance equation is the air drag force, which becomes increasingly important at high spinning speeds. Numerous theoretical and experimental investigations have focused on identifying the nature of the drag coefficient C_d , in the drag force equation. To evaluate C_d for melt spinning, Sakiadis (23) used boundary layer analysis to calculate the drag coefficient as

$$C_d = 4/(\beta \text{Re}) \quad [2.1.6]$$

Where the parameter β was developed by integrating from 0 to β using

$$\xi^2 = 8 \int_0^\beta \frac{(z-1) \exp(2z) + z^2 + 1}{z^2} dz \quad [2.1.7]$$

and $\xi^2 = \frac{64 \text{Re } z}{D}$

This approach for calculating drag force was used in the mathematical model developed by Ziemiński (13,14).

In a simpler approach, correlation with the air Reynolds number, $(\rho_a U D / \mu_a)$, is nearly always assumed. In high speed spinning, the boundary layer on the filament should be turbulent. Matsui (24) has formulated a simple expression for C_d based on air Reynolds number using turbulent theory

$$C_d = K Re^{-n} \quad [2.1.8]$$

where $K=0.37$ and $n=0.61$. Although the data reported by many previous investigators, as summarized by Shimizu et al. (15), are very scattered; the exponent n lies mostly in the range of 0.6-0.8. The values of n and K are strongly dependent on the way in which a straight line is drawn in the log-log plot of C_d versus Re .

Shimizu et al. (25) indicate the limited importance of air drag for structure formation as compared to inertial forces. They consider two sections of the spinline; the deformation section and the downstream section after solidification. In the deformation section inertial forces are predominant and air drag plays a secondary role in the balance of forces. Most of the structure development takes place in the deformation section while skin friction is dominant in the downstream section of the spinline. Thus it is the inertial force which plays the dominant role in the formation of fiber structure.

2.2 Melt Rheology and Constitutive Equations

The axial stress in the spinline and hence, the rheological force is related to the kinematics of the spinline (deformation, deformation rate, etc.) through the rheological constitutive equations.

For incompressible materials such as polymer melts the deformation of the material does not determine the stress tensor uniquely, since any isotropic pressure may

be added to it without any effect on the deformation. Thus the total stress tensor σ_{ij} is split-up into an isotropic stress tensor $P\delta_{ij}$ (equal to hydrostatic pressure only in a stationary fluid) and deviatoric stress tensor (or an extra stress tensor) T_{ij} as follows:

$$\sigma_{ij} = -P\delta_{ij} + T_{ij} \quad [2.2.1]$$

where δ_{ij} is a Kroneker delta and is defined to be equal to one when $i=j$ and zero when $i \neq j$.

The basic variable is then the extra stress tensor T_{ij} and is related to the kinematics of the flow (deformation, deformation gradient, etc.) through the rheological constitutive equations. Rheology of polymers has developed during the last forty years into a wide branch of theoretical and experimental science.

The simplest rheological constitutive equation is the Newton's law of viscosity, rigorously stated as (26)

$$T_{ij} = \mu d_{ij} \quad [2.2.2]$$

where, T_{ij} = the deviatoric stress tensor
 d_{ij} = the deformation rate tensor
 $= (\partial u_i / \partial x_j + \partial u_j / \partial x_i)$
 μ = deformation rate independent viscosity

For simple shear flow, equation [2.2.2] becomes $T_{xy} = T_{yx} = \mu \gamma$, (γ is shear rate and μ becomes shear viscosity), a form in which Newton's law of viscosity is usually stated in an elementary treatment of fluid mechanics.

Although simple shear flow has been most widely studied, the occurrence of

elongational flow in polymer processing operations such as melt spinning, film blowing and melt blown fabric processing makes it an important area of study (27-29). The stress accompanying the extension of the material is of particular importance in defining operating conditions for such processes. For this reason one defines an uniaxial elongational viscosity η_e (sometimes called a tensile viscosity) as

$$\eta_e = \sigma_{11}/\dot{E} \quad [2.2.3]$$

where $\dot{E}$ is the elongation rate. Note that η_e is defined in terms of the total stress σ_{11} and not in terms of the deviatoric stress T_{11} . As early as 1906, Trouton (30) showed that the uniaxial elongational viscosity (hereafter to be referred to as elongational viscosity) of a Newtonian fluid is three times the shear viscosity. This result is mathematically similar to the result that the Young's modulus for an incompressible isotropic Hookean solid is three times the shear modulus.

The viscosity of most polymers changes greatly with temperature. For Newtonian liquids and for polymer fluids at temperatures far above the glass transition temperature T_g , the viscosity follows the Arrhenius equation to a good approximation (31),

$$\eta = K e^{A/RT} \quad [2.2.4]$$

where K at a given shear stress is a characteristic of the polymer and its molecular weight, A is the activation energy for the flow process, R is the gas constant and T is the absolute temperature (Kelvins). The activation energy generally is in the range between 5 and 50 Kcal/mole (31). The energy of activation for flow increases as the size of the side groups increases and as the chain becomes more rigid.

For amorphous polymers at temperatures less than 100 °C above their T_g , the Arrhenius equation does not fit the data well. A much better equation is the Williams-Landel-Ferry (or WLF) equation (31)

$$\text{Log}_{10}\left(\frac{\eta}{\eta_g}\right) = \frac{-c_1(T - T_g)}{c_2 + (T - T_g)} - \text{Log}_{10}\left(\frac{T_g \rho_g}{T \rho}\right) \quad [2.2.5]$$

$$\text{For } T_g < T < T_g + 100$$

The viscosity at T_g at low rates of shear is η_g , T is the absolute temperature in Kelvins, ρ is the density at that temperature, and ρ_g is the density at T_g . The term $\text{log}_{10}(T_g \rho_g / T \rho)$ is generally near zero. The viscosity at T_g is often about 10^{13} poise. The Arrhenius equation is generally satisfactory if the temperature is greater than $(T_g + 100^\circ\text{C})$; at the lower temperatures, the WLF or similar type of equation with an adjustable empirical value of reference temperature instead of T_g should be used.

Isothermal spinning experiments can separate the basic rheological response of the material from the temperature dependence of its behavior and are required for any fundamental study of polymer melts. Patel and Bogue (32,33) have studied the isothermal elongational behavior of low molecular weight polypropylenes using the gravity spinning method. The isothermal Newtonian spinning theory as extended by Patel and Bogue (33) provides a base case to understand and analyze the isothermal spinning experiments. They also analyzed and simulated the dynamics of the isothermal spinline using appropriate viscoelastic models in the differential form. Such experiments, coupled with the heat transfer studies and non-isothermal rheology, offers a more reliable understanding of the nonisothermal fiber spinning process.

The spinline flow is not spatially homogeneous in that the stress and the strain rate

vary along the spinline (34). The flow is steady in the Eulerian sense in that at any point in the spinline the velocity of the fluid is constant. However, a particle of the fluid will experience a changing velocity and velocity gradient as it moves along the spinline; in other words the flow is unsteady in the Lagrangean sense. For viscoelastic polymer melts, the elongational viscosity at any point in the spinline depends not only on temperature but also on the elongation rate at that point ($=dV/dz$) and the history of prior deformation. The elongational viscosity in fiber spinning is, therefore, termed as an apparent elongational viscosity. We note that it is not a fundamental material parameter but is an unsteady-state parameter. However, it is a convenient parameter to represent the spinning data. Transient viscoelastic effects in molten polymers are typical for elongational flow. This will be especially true for spinning of melts having significant elastic response and at higher spinning speeds. Thus one requires a viscoelastic constitutive equation to describe the rheological response of such materials in fiber spinning.

As noted above most previous researchers have assumed that the Newtonian constitutive equation describes adequately the rheological response of the polymer in fiber-spinning. Under this assumption, the elongational viscosity of the melt is taken to be dependent only on temperature. However, polymer melts are viscoelastic fluids: like viscous liquids, they flow; but they also show elastic or memory effects, in that the present stress state depends on the previous history of deformation. Normally, the effect of temperature on viscosity is known to be strong and cooling rates in the spinline are generally high. Hence in the case of melt spinning of relatively inelastic melts such as nylons and polyesters, the temperature effects on viscosity override the viscoelastic effects. In such cases it is reasonable to describe the spinline rheological behavior with a temperature dependent Newtonian viscosity. However, for highly elastic (and

deformation rate thinning) melts such as polyethylenes, a purely viscous constitutive equation [2.2.2] would no longer be adequate because of strong viscous-thinning and elastic (or time) effects.

Viscoelasticity theory, which originated in one dimensional mechanical models for small strains, has been generalized to three dimensional, large deformation theories, the rheological constitutive equations. The constitutive equation used to describe the rheological behavior of a viscoelastic liquid is the key to any analysis of how the material flows. Constitutive equations are formulated in two different ways: a differential type formulation and an integral type formulation. Constitutive equations, either in differential form or in integral form, can be used for the interpretation of spinning data. For integral models, a calculation of the stress evolution requires a knowledge of the kinematics upstream and into the nozzle, or spinneret; spinneret kinematics are very complex and can only be approximated (35,36). A problem in applying integral equations in process design is that the material being deformed will seldom begin the deformation process of interest in its "virgin" (stress-free) state, and the upstream deformation history will seldom be known accurately. Also, the prediction of stress using such integral constitutive equation requires a double integration to be performed and hence requires a large amount of computing time.

Derivative type constitutive equations circumvent many of these difficulties, since the material memory is introduced in a manner dependent only on the local values of stress, deformation rate, and the derivatives of these quantities. Using the differential models, the simulation of non-isothermal fiber spinning requires a numerical solution of first order ordinary differential equations, relating extra stress tensors T_{11} and T_{22} , along with differential force balance and energy balance equations.

Differential formulations : The historical development of the differential type constitutive

equation is based on the classical "Maxwell model", which consists of a viscous element (dashpot) and an elastic element (elastic spring) in series. The simplest derivative-type model is any of several variations of the convected Maxwell equation :

$$T_{ij} + \tau(\delta T_{ij}/\delta t) = G\tau d_{ij} \quad [2.2.6]$$

where d_{ij} is a deformation rate tensor ($d_{ij} = dv_i/dx_j + dv_j/dx_i$), G is a shear modulus, τ is a relaxation time. $(\delta T_{ij}/\delta t)$ denotes any suitable time derivative which moves and deforms or rotates with a fluid element. Three convected time derivatives which satisfy the principle of material objectivity are the contravariant and covariant formulations of the Oldroyd derivative (37), and the Jaumann derivative discussed by Oldroyd (38) and Prager (39). Of the three convected time derivatives, the contravariant formulation possesses the correct characteristics of predicting high stress levels in elongational flows and a finite first normal stress difference and zero second normal stress difference in shear flow. Experimental data show a second normal stress difference which is about -0.2 to -0.3 times the first normal stress difference (40,41), but the approximation of a zero second normal stress difference is still often used. A zero second normal stress difference is also predicted by a number of molecular theories. Thus, if eq. [2.2.6] is to be used, the choice of the contravariant time derivative appears to be the most realistic one. Ziabicki (21,42) used the Jaumann time derivative leading to co-rotational Maxwell model even though the predictions of the co-rotational Maxwell model do not conform to the experimental results obtained in shear and elongational flow.

A convected Maxwell model with the Oldroyd contravariant derivative gives the following predictions in simple shear :

$$T_{12} = G\tau\dot{\gamma}$$

$$N_1 = T_{11} - T_{22} = 2G\tau^2\dot{\gamma}^2 \quad [2.2.7]$$

$$N_2 = T_{22} - T_{33} = 0$$

Note that the model predicts constant viscosity and zero second normal stress difference in shear and the first normal stress difference is predicted to be proportional to the square of the relaxation time and the shear rate.

Bogue-White model : The convected Maxwell model with a contravariant time derivative predicts a constant viscosity, independent of shear rate, while it is known experimentally that both the viscosity and the relaxation time are decreasing functions of shear rate. This dependence has generally been introduced by making these parameters functions of the second invariant of the deformation rate tensor, as in the Bogue-White model (43,44). The Bogue-White model in differential form is the same as the convected Maxwell model with a contravariant time derivative with τ_n replaced by τ_{neff} where, τ_{neff} is an effective (deformation rate dependent) relaxation time given by

$$\tau_{neff} = \frac{\tau_n}{1 + \left(a \tau_n \left\langle \pi_d^{1/2} \right\rangle \right)^b} \quad [2.2.8]$$

where "a" is a thinning parameter and "b" is an adjustable (empirical) factor to obtain the correct asymptotic slope of the viscosity-shear rate curve at large shear rates. The parameter $a=0$ corresponds to the convected Maxwell model. The Bogue-White model, when originally proposed, assumed the value of this adjustable factor "b" to be unity, which did not have the correct asymptotic slope of viscosity-shear rate curve at large

shear rates. For this modified Bogue-White model, the value of "b" usually lies between 0.75-0.8. $\langle \pi_d \rangle$ is the second invariant of the deformation rate tensor. In simple shear, $\langle \pi_d^{1/2} \rangle$ is just the shear rate γ , while in uniaxial elongation it is $\sqrt{3}E$. The Bogue-White model with $b=1$, both in differential and integral form has been found to successfully correlate data on bulk polymers (45-50).

Nonisothermal rheology: The rheological response of polymers has been extensively studied under isothermal conditions and several constitutive models reproduce the main features experimentally observed. However much less attention has been given to the field of nonisothermal rheology. In this field stress response under conditions of simultaneous deformation and temperature changes is studied. The importance of these studies is evident from the fact that nonisothermal histories occur in almost all polymer processing operations. (Generally the material is moved and shaped as a melt and then cooled, usually quite rapidly, to a solid state.) However there have been only a few theoretical analyses and even fewer experimental studies reported in the literature.

Frequently the constitutive equations derived under isothermal conditions are extended to account for temperature variations by employing the concept of thermorheological simplicity first suggested by Morland and Lee (51). The principal of time-temperature superposition provides the basis for this understanding by relating rheological properties measured at one temperature to those measured at another. However, the formulation of this principal and its justification by overwhelming experimental evidence are for isothermal flows only. Markovitz (52) has questioned the theoretical basis of the thermorheological simplicity assumption and it can't be presupposed to be valid in nonisothermal conditions. But for simplicity and convenience, the basic building block of many approaches in the literature has been thermorheological simplicity.

In 1977, Matsui and Bogue (35) introduced this concept in a nonisothermal constitutive equation for polymer melts. They modified the integral BKZ constitutive equation (53) by using reduced time as,

$$\sigma_{ij} = -p\delta_{ij} + \int_{-\infty}^t \sum_n G_n \frac{\exp\left[-\int_t^{t'} \frac{dt''}{\tau_n(t'')}\right]}{\tau_n(t')} C_{ij}^{-1} dt' \quad [2.2.9]$$

where C_{ij}^{-1} is a Finger strain tensor.

Thus this theory evolves from isothermal theory in a natural way and has a good foundation of well proven reduced time concept.

The form of the Maxwell model which is appropriate for nonisothermal conditions has been shown by Marrucci (54) to be

$$T_{ij} [1 - \tau D(\ln T)/Dt] + \tau \delta T_{ij}/\delta t = G t d_{ij} \quad [2.2.10]$$

where d_{ij} is the deformation rate, $\delta/\delta t$ is the Oldroyd contravariant convected time derivative, D/Dt is the material time derivative, T_{ij} is the deviatoric stress, T is the temperature and τ is relaxation time. The relaxation time τ can be a function of both temperature and deformation rate. The temperature dependence is introduced by appropriate shift factor using the thermorheological simplicity assumption. The deformation rate dependence can be introduced using the Bogue-White model. The term $D(\ln T)/Dt$ does not contribute significantly to the stress development and is usually neglected (10).

This theory is not complete and doesn't exactly predict the experimentally observed rheological behavior of amorphous polymer melts near their glass transition

temperature. However, the theory is adequate for predicting nonisothermal viscoelastic response well above the glass transition temperature.

2.3 Energy Balance

In non-isothermal melt spinning an energy balance is required to determine the fiber temperature as a function of distance (or time) from the spinneret. Heat transfer from the melt spinline to the ambient medium involves several mechanisms: radiation, free convection and forced convection. The effect of radiation is strongly dependent on the temperature of the fiber. In melt spinning of inorganic glasses or metals, where extrusion temperatures reach 900-1300 °K, the contribution of radiative heat transfer is considerable. Because the melt temperature of polymers is generally less than 300 °C, the radiation contribution is usually negligible compared to the convective heat transfer. Heat released due to crystallization can be neglected for slowly crystallizing polymers such as nylons and polyesters at slow to medium speed spinning. But at high speeds, high rates of crystallization due to stress induced crystallization are obtained in these polymers and heat of crystallization should be considered in the heat balance. The heat of crystallization should also be considered for fast crystallizing polymers such as polyethylenes and polypropylenes. Neglecting radial temperature variations and including heat of crystallization, the differential energy balance equation becomes (17)

$$\frac{dT}{dz} = - \frac{\pi D h (T - T_a)}{W C_p} + \frac{\Delta H_f}{C_p} \frac{dX}{dz} \quad [2.3.1]$$

where T is the fiber temperature, T_a is the ambient temperature, ΔH_f is the heat of fusion, X is the crystalline fraction, h is the heat transfer coefficient, and C_p is the resin heat

capacity.

The key parameter in calculating the temperature profile of the spinline is the heat transfer coefficient, h . There have been many attempts to provide theoretical and empirical relationships describing h as a function of spinning conditions through use of dimensionless groups such as Nusselt (Nu), Reynolds (Re), Prandtl (Pr) and Grashof (Gr) Numbers.

Free or natural convection, associated with the motion of the ambient medium in the temperature field around the cooling filament, is the typical heat transfer mechanism for a stationary system, and it may prevail in melt spinning at very low take-up speeds. In this case

$$Nu = Nu(Gr, Pr) \quad [2.3.2]$$

Natural convection is not expected to be important at medium to high spinning speeds, in which case the Nusselt number should be a function of the Reynolds number only. Correlations for heat transfer into quiescent air are of the form

$$\frac{hD}{k_{\text{air}}} = \delta \left(\frac{\rho_{\text{air}} VD}{\mu_{\text{air}}} \right)^a \quad [2.3.3]$$

where, " a " ranges between 0.2 and 0.5. Ziabicki (21) has summarized various expressions relating heat transfer coefficient to processing variables. Kase and Matsuo (7) gives $a=1/3$ and $\delta=0.42$ with data taken for air blown past a stationary cylinder. They also included the effect of air flow normal to the fiber axis (cross-current of air), and the final form is

$$\frac{hD}{k_{\text{air}}} = 0.42 \left(\frac{\rho_{\text{air}} VD}{\mu_{\text{air}}} \right)^{1/3} \left[1 + 8 \left(\frac{u_c}{V} \right)^2 \right]^{1/6} \quad [2.3.4]$$

where u_c is the cross-air flow velocity.

2.4 Crystallization Kinetics

Crystallization is the process whereby an ordered structure is produced from a disordered phase, usually a melt or dilute solution. In semi-crystalline polymer processing, crystallization is the most important phase transition, e.g. in molding, film blowing and melt spinning of fibers. In the case of spinning the time dependent changes in degree of crystallinity affects heat transfer, rheological properties of the polymer and, consequently, the kinematics and dynamics of spinning. Of particular significance is the effect on fiber structure. Knowledge of the nucleation rate, growth rate, and growth morphology are essential to a full understanding of crystallization. Direct observation of the process of spherulitic growth helps in elucidating the mechanism of crystallization and subsequent development of morphology. However, the rate of phase transformation of polymers from amorphous to the crystalline phase, called the bulk crystallization rate, is a useful macroscopic parameter for analysis of polymer crystallization.

Crystallization in a polymer processing operation almost invariably occurs under nonisothermal conditions and frequently in the presence of molecular orientation. The mathematical modeling of crystallization for such processes requires a nonisothermal description of crystallization and a knowledge of crystallization rate as a function of temperature and molecular orientation. Crystallization rates are usually measured under quiescent, isothermal conditions, and, in many cases, they are experimentally accessible only over a narrow temperature range at low undercoolings-- a temperature range that is

often well above that where crystallization occurs in processing. This raises the question of how crystallization rates measured under isothermal conditions can be applied to nonisothermal processes. Measurement of nonisothermal quiescent crystallization using common experimental techniques such as differential scanning calorimetry (DSC) is possible only at low cooling rates; much lower than is found in most processes. Hence, a procedure, preferably based on theory, is required to describe and extrapolate either isothermal or nonisothermal measurements of crystallization.

Isothermal kinetics : The isothermal rate at which the total amount of crystallinity develops in a pure homopolymer follows an almost universal pattern first observed by Bekkedahl (55) in his study of natural rubber. In such experiments, when the polymer sample is quickly transferred from a temperature above the melting temperature to the predetermined crystallization temperature, characteristic sigmoidal-shaped isotherms are obtained. The time taken for half the crystallization to develop ($t_{1/2}$, a measure of crystallization rate) is a strong function of crystallization temperature. At temperatures in the vicinity of the melting temperature (T_m) the crystallization rate is very slow. As the temperature is lowered, the rate progressively increases and eventually passes through a maximum. At crystallization temperatures below the maximum, the over-all rate of crystallization becomes small again. For many polymers, however, the rate becomes so rapid at temperatures below T_m that it is extremely difficult to study isothermal crystallization experimentally and to detect the temperature at which the rate is a maximum.

An impressive body of experimental evidence, for a variety of polymers, demonstrates that at fixed temperature the radius of a growing spherulite increases linearly with time over a wide range of crystallization temperatures (56). Also, the temperature variation of the spherulitic growth rate, G , is qualitatively similar to the temperature

coefficient of the over-all rate of development of crystallinity. The basic equation describing the temperature dependence of growth rate of polymer crystals reads as follows (57):

$$G = G_0 \exp(-E_{\text{act}}/RT) \exp(-\Delta W^*/kT) \quad [2.4.1]$$

where E_{act} is the activation energy for the transport process at the interface, W^* is the work required to form a crystal nucleus of critical size, R is the universal gas constant and k is the Boltzmann constant.

Hoffman proposed the following particular relations for the growth rate (58-61):

$$\frac{E_{\text{act}}}{RT} = \frac{c_1}{R(c_2 + (T - T_g))} = \frac{U^*}{R(T - T_\infty)} \quad (\text{WLF formulation}) \quad [2.4.2]$$

$$\frac{\Delta W^*}{kT} = \frac{Y b_o \sigma \sigma_e T_m^0}{k \Delta h_m T \Delta T f} = \frac{K_g}{T (T_m^0 - T) f} \quad [2.4.3]$$

where Y = Regime dependent parameter (=4 in Regime III)

b_o = thickness of the chain molecules

σ = interfacial free energy (per unit area) parallel to the chain

σ_e = interfacial free energy (per unit area) perpendicular to the chain

Δh_m = heat of melting per unit volume

T_m^0 = equilibrium melting point

f = correction term that accounts for the change in Δh_m with large undercoolings.

$$= 2T/(T_m^0 + T)$$

The factor $\exp\{-U^*/R(T-T_\infty)\}$ is usually thought of as representing the temperature dependence of the segmental jump rate in polymers; this factor also governs the variation of viscosity of molten polymers between T_g and T_g+100 °K. The absolute value of the viscosity depends on additional factors, such as molecular weight, which enters as $M_w^{3.4}$. The jump rate does not depend strongly on the molecular weight. The temperature T_∞ is a hypothetical temperature where all motion associated with viscous flow ceases, and it is related to the glass transition temperature of the polymer. Though considerable departures from the "universal" values are known to occur, the quantity U^* correlating viscosity data is generally within 10-15 % of 4100 cal/mole and T_∞ is usually within about 5-10 °K of being 50 °K below T_g . The values of U^* and T_∞ that apply to the crystallization process need not, however, be exactly the same as those that apply to bulk viscosity; they probably refer to motions near and within a physically adsorbed layer of molecules that exists on the surface of the crystals. Several authors (62,63) have tried to apply a temperature independent energy of activation, specific to a given polymer. However, this Arrhenius type approximation for the transport term does not correlate the growth rate data well, especially over a wider range of temperatures and at high undercoolings (64). Some of the researchers have argued that crystallization in polymers should not be modeled as a single step process. They argue that initial crystallization (with variable length of chain stem) is invariably followed by annealing or crystal perfection with a different kinetics. In view of recent confirmation of the concept of non integral folding (NIF) during crystallization, the parameter K_g in Hoffman's theory (which assumes constant kinetic length of chain stem) should probably be considered more or less as an empirical parameter.

The knowledge of the linear growth rate and the primary nucleation rate should be sufficient to calculate the overall crystallization rate. Many measurements of crystallization, however, involve the macroscopic determination of crystallinity as a function of time e.g. using light depolarization microscopy, dilatometry, DSC, etc. The first efforts to describe quantitatively the macroscopic development of crystallinity in terms of nucleation and linear crystal growth were made by Kolmogoroff (65), Johnson and Mehl (66) and Avrami (67). Evans (68), seemingly without knowledge of prior work, developed similar descriptions, based on the old problem of expanding waves created by raindrops on a pond, first solved by Poisson in 1837. The degree of phase transformation, $X(t)$, is related to time t by the general Avrami equation

$$X(t) = 1 - \exp(-kt^n) \quad [2.4.4]$$

where k is the crystallization rate constant containing nucleation and growth rates, and n is a constant called the Avrami index, characteristic of the nucleation mode (sporadic or instantaneous) and the crystal growth geometry (rod, disk, sphere, etc.). Values of parameters k and n can be obtained by fitting isothermal kinetics data, obtained by suitable method for following development of crystallinity. Theoretically, a plot of $\ln[-\ln(1-X/X_\infty)]$ versus $\ln(t)$ should be linear with n being the slope and $\ln(k)$ being the Y-intercept (69). However, the intercept obtained by linear regression may not be statistically accurate. Therefore, the rate constant k is frequently evaluated from the half-time of crystallization ($t_{1/2}$) using $k = \ln(2)/t_{1/2}^n$ where n is the Avrami index. The general problem of interpretation of experimental data using the Avrami equation is that fractional exponents from data fitting is more usual than exceptional. Also, the experimental data frequently deviate at long crystallization times, showing slower increases in the crystallinity than expected from the initial data. As stated by Wunderlich (70), the

exponent n in the Avrami equation [2.4.4] may show values ranging from below 1 to far above 6. Any one value, whole or fractional, however, is not uniquely fixed to any one set of conditions. Additional information on nucleation, morphology, and possibly even mechanism is necessary to fully interpret the exponent n . Without the parallel knowledge of the microscopic, independently proven mechanism, the macroscopic Avrami parameters are only a convenient means to represent empirical data of crystallization.

Recently, Khanna and Taylor (71) have indicated that the values of k and activation energy, A , obtained using the Avrami equation [2.4.4] may not be meaningful. They found k to be a function of the Avrami exponent " n ", although this is not explicitly revealed by the Avrami equation [2.4.4]. They suggested a modified Avrami equation,

$$X(t) = 1 - \exp[-(kt)^n] \quad [2.4.5]$$

They claim that this equation retains the original correspondence of the Avrami equation to nucleation and crystal growth processes, but extends its applicability to (i) correctly evaluate k and A parameters, and (ii) correctly compare transformation rates when the systems differ in their n values. They have presented experimental data to support their conclusions.

The Avrami analysis reported above neglects a slow secondary crystallization process occurring during isothermal crystallization. Many previous reports consider the use of two Avrami equations dealing with primary and secondary crystallization separately. Banks et al. (72) describe a procedure to treat the primary and secondary crystallization processes separately whether they occurred "consecutively or concurrently". Price (73) considered an integral form of the Avrami equation in 1965 to describe secondary crystallization in intra-spherulitic material. Hiller (74) proposed a

modified Avrami equation consisting of two consecutive processes, with the second process varying linearly with $\ln(\text{time})$. In 1971, Booth and Hay (75) analyzed polyethylene using the modified dual Avrami equation of Banks (72). They concluded that the first, or primary, crystallization process resulted in fractional Avrami exponents. In the parallel Avrami model used recently by Velisaris and Seferis (76), two Avrami equations are used to describe bulk crystallization that occurs via two simultaneous processes. The model is applied to isothermal and nonisothermal crystallization of both neat resin and composite poly(ether ether ketone) (PEEK). In their parallel Avrami model, the relative degree of crystallinity during isothermal crystallization at temperature T is written as:

$$X_c/X_c(\infty) = w_1[1 - \exp(-k_1(T)t^{n_1})] + w_2[1 - \exp(-k_2(T)t^{n_2})] \quad [2.4.6]$$

where, for the i th process ($i=1, 2$), w_i is the weight fraction and k_i and n_i are, respectively, the Avrami rate parameter and exponent. The sum of the weight fractions is $w_1 + w_2 = 1$.

Dietz (77) has proposed an additional term into the isothermal rate of crystallization equation (differential form of Avrami equation [2.4.4]) to account for the slow secondary crystallization. His modified rate of crystallization equation is given as follows:

$$\frac{d\theta}{dt} = n k t^{n-1} (1 - \theta) \exp\left(\frac{-a\theta}{1-\theta}\right), \quad a \geq 0 \quad [2.4.7]$$

where $\theta = X(t)/X_\infty$ and the parameter "a" lies above zero and its value increases with increasing proportion of secondary crystallization. This parameter can be estimated by

fitting the isothermal crystallinity data, especially towards the end of crystallization. For isothermal crystallization, $a=0$ leads the above equation to the familiar Avrami equation in one of its differential form.

For many polymers, it is possible to measure quiescent isothermal crystallization rates only over a narrow temperature range, at low supercoolings. At high supercoolings isothermal rates becomes too rapid to follow development of crystallinity by presently available techniques. Under high cooling rates, crystallization occurs at low temperatures. Thus, the experimentally obtained macroscopic rate of crystallization needs to be extrapolated to lower temperatures (high supercoolings) where crystallization usually occurs in processing of semi-crystalline polymers.

Ziabicki (21) has proposed an empirical equation for the temperature dependence of the experimentally observed crystallization half times $t_{1/2}$ as follows:

$$\left(\frac{1}{t_{1/2}}\right) = \left(\frac{1}{t_{1/2}}\right)_{\max} \exp \left[-4 \ln(2) \frac{(T - T_{\max})^2}{D^2} \right] \quad [2.4.8]$$

where $(1/t_{1/2})_{\max}$ is the maximum in the rate-temperature curve, $T_{\max}$ is the temperature at $(1/t_{1/2})_{\max}$ and D is the half-width of the rate-temperature curve. $T_{\max}$, $(1/t_{1/2})_{\max}$ and D can be determined from measured half-times, using a non-linear regression method. However, as mentioned above, the isothermal kinetics data are usually available in a very narrow temperature range at low supercoolings. Hence, the value of the three parameters obtained by non-linear regression from few experimental data points would not be accurate. Therefore, one needs to resort to an expression based, at least partially, on the theory for the required extrapolation.

Velisaris and Seferis (76) in their attempt to model non-isothermal crystallization

kinetics of composite PEEK, assumed that growth rate (G) is temperature independent and temperature dependence of $k(T)$ is completely determined by the temperature dependence of the rate of homogeneous nucleation, $N(T)$. However, the assumption of homogeneous nucleation in polymer, and certainly in case of fibrous composite is not justifiable. Also, Cebe (78) was not able to fit her data on PEEK composite, using the expression for $k(T)$ based on this assumption. Instead, she (78) assumed that $k(T)$ may be determined mainly by the temperature variation of linear growth rate $G(T)$ and not by the rate of nucleation.

Assuming that the number of heterogeneous nuclei is not strongly temperature dependent, and all sites become active simultaneously and noting that the most general form of $k(T)$ requires $G(T)$ to be raised to the n -th power, Cebe (78) used the following expression for the temperature dependence of $k(T)$:

$$k(T) \approx G(T)^n$$

[2.4.9]

$$k(T) = C_1 \exp \left[- \frac{C_2}{(T - T_g + 51.6)} \right] \exp \left[- \frac{C_3}{T \Delta T f} \right]$$

All prefactors, including the number of nuclei, have been lumped together in C_1 .

The Hoffman-Lauritzen theory (61) gives the temperature variation of linear spherulitic growth rates. Data on the rate of bulk crystallization can also be used in the Hoffman-Lauritzen theory (59,79). For heterogeneous nucleation with spherulitic growth, the Avrami rate constant k is equal to $4\pi n_0 G^3/3$, where n_0 is the number of heterogeneous nucleation centers (spherulitic centers) per unit volume and G is the linear growth rate. Hence value of C_3 can be obtained from the slope of the plot of $1/3 \ln(k/n_0) + U^*/(R(T-T_\infty))$ versus $1/(T\Delta T)$ (59). It can be shown that $(1/t_{1/2})$ (a measure of

crystallization rate) is proportional to growth rate G , if number of heterogeneous nuclei is assumed to be relatively independent of temperature and all sites become active simultaneously. The temperature variation of $t_{1/2}$ can then be written using Hoffman-Lauritzen theory (79) as follows:

$$\frac{1}{t_{1/2}} = \left(\frac{1}{t_{1/2}} \right)_0 \exp \left[- \frac{U^*}{R(T - T_\infty)} \right] \exp \left[- \frac{C_3}{T \Delta T f} \right] \quad [2.4.10]$$

where $T_\infty = T_g - 30^\circ\text{K}$ and U^* is the activation energy for segmental jump rate in polymers. The correction factor f accounts for decrease in latent heat of fusion Δh as temperature is lowered and is approximately equal to $2T/(T + T_m^0)$. The above expression can be used to obtain the values of $(1/t_{1/2})_0$ and C_3 from the plot of $\ln(1/t_{1/2}) + U^*/(R(T - T_\infty))$ versus $1/(T \Delta T)$ (73,74). Equation [2.4.10] can be used even if nucleation density changes with temperature. In this case work on polypropylenes by Hammami (80) has shown that the C_3 term does not have the same fundamental significance as in the growth rate theory and was higher than the value that was obtained from application of Hoffman's analysis to spherulitic growth rate data for polypropylene (80). Knowing the value of $(1/t_{1/2})_0$ and C_3 , the half time values can be extrapolated to lower temperatures, from which Avrami rate constant k can be calculated. The half-time analysis approach is a better method to correlate quiescent kinetics data of a given resin than the empirical Ziabicki equation [2.4.8]. It must be mentioned, however, that very large extrapolations will be questionable using any procedure. This fact emphasizes the need to develop experimental techniques for studying crystallization rates at high undercoolings.

Non-isothermal kinetics : The general Avrami theory of phase change can be extended as to describe nonisothermal kinetics. Under cooling conditions, nucleation

sporadic as the number of activated heterogeneous nuclei is usually temperature dependent. The general Avrami theory for three-dimensional spherulitic growth then can be written as (81):

$$\frac{X(t)}{X_{\infty}} = 1 - \exp \left[- \frac{\rho_c}{\rho_l} \int_0^t \mu(\tau) \frac{4\pi}{3} \left(\int_{\tau}^t G(x) dx \right)^3 d\tau \right] \quad [2.4.11]$$

where $\mu(\tau)$ is the rate of sporadic nucleation at time τ . In principle, knowing nucleation rate and growth rate as a function of temperature, one can calculate nonisothermal crystallinity under arbitrary cooling conditions. However, it is tedious to obtain these data and the above general equation is then simplified to obtain more tractable models to deal with nonisothermal crystallization.

Under the simplifying assumption of constant cooling rate, Ozawa (82) has extended the Avrami equation to nonisothermal crystallization, following the mathematical derivation of Evans (68). According to Ozawa theory, the degree of conversion at temperature T amounts to:

$$\ln(1 - X_T/X_{\infty}) = k(T)/R^n \quad [2.4.12]$$

where X_{∞} is crystallinity at the termination of the crystallization process, X_T is crystallinity at temperature T , R is cooling (or heating rate), $k(T)$ is cooling or heating function. The integer n has a value between 1 and 4 depending on whether nucleation is instantaneous or sporadic, and on the number of dimensions in which growth occurs. It can be noted that the Ozawa equation can also be easily obtained from equation [2.4.11] under constant cooling rate.

The Ozawa equation [2.4.12] has been tested for PET and nylon-6 crystallization

(82,83). The analysis requires values of relative crystallinity at a given temperature for different cooling rates. Hence, it is not possible to include a wide range of cooling rates and the temperature range over which analysis can be applied is very narrow. Eder and Wlochowicz (84) found it to describe nonisothermal crystallization of isotactic polypropylene though the Ozawa exponent varied from 3.3 to 2.6 with temperature. They found that cooling crystallization of polyethylene did not follow the Ozawa equation, probably because of factors neglected in the theory of Ozawa such as secondary crystallization. Monasse and Haudin (85) have used the Ozawa theory to interpret the type of nucleation and to predict the thermal dependence of the spherulitic growth rate (K_g) for polypropylene by nonisothermal calorimetry. However, their classification of nucleation types under nonisothermal conditions seems to be flawed. They also assumed instantaneous nucleation (all nuclei being activated at $T=T_m$), which is not true for polypropylene (80), to compute K_g . Lopez and Wilkes (86) have also used the Ozawa method to analyze nonisothermal kinetics data of poly(p-phenylene sulphide) obtained using a Perkin-Elmer DSC-4.

Nakamura et al. (81) have simplified equation [2.4.11] by introducing a characteristic time. The assumption of the isokinetic condition (i.e. ratio nucleation rate and growth rate is constant independent of temperature) and independence of the ultimate crystallinity on the cooling process led to the following equation :

$$\frac{X(t)}{X_{\infty}} = 1 - \exp \left[- \left(\int_0^t K(T) dt \right)^n \right] \quad [2.4.13a]$$

or using temperature as an independent variable, it reads:

$$\frac{X(T)}{X_{\infty}} = 1 - \exp \left[- \left(\int_{T_0}^T K(T) \frac{dT}{R} \right)^n \right] \quad [2.4.13b]$$

where $X(t)$ is the degree of phase transformation at time t , $X(T)$ is the degree of phase transformation at temperature T , R is the cooling rate, n is the Avrami index determined in the isothermal experiments, and $K(T)$ is related to the isothermal crystallization rate through the relation $K(T)=k(T)^{1/n}$. It is interesting to note that equation [2.4.13a] or [2.4.13b] can also be obtained as an empirical nonisothermal expression of the modified statement of the isothermal Avrami equation [2.4.5] suggested by Khanna and Taylor (71). In many instances of modeling, a differential form of Eq. [2.4.13] is useful. It reads as follows:

$$\frac{d\theta}{dt} = n K(T) (1 - \theta) \left[\ln \left(\frac{1}{1 - \theta} \right) \right]^{\frac{n-1}{n}} \quad [2.4.14]$$

where $\theta = X(t)/X_{\infty}$. The integral and the differential Nakamura model are identical in terms of their predictions. Note, however, that differential equation [2.4.14] requires a non-zero initial crystallinity condition for $n > 1$ (if $\theta=0$ then $d\theta/dt=0$).

Apparently unaware of the Nakamura model, Kamal and Chu (87), Velisaris and Seferis (76) and Cebe (78) have used an empirical integral Avrami expression to describe nonisothermal primary crystallization. This expression hereafter will be referred to as the Kamal model. It reads as follows:

$$\frac{X(t)}{X_{\infty}} = 1 - \exp \left[- \int_0^t k(T) n t^{n-1} dt \right] \quad [2.4.15a]$$

or using temperature as an independent variable, for constant cooling rate, it reads:

$$\frac{X(T)}{X_{\infty}} = 1 - \exp \left[- \int_{T_0}^T k(T) n \left(\frac{T_0 - T}{R} \right)^{n-1} \frac{dT}{R} \right] \quad [2.4.15b]$$

Both the Nakamura model and the Kamal model do transform back to the Avrami equation under isothermal conditions. It can also be noted that the model equations [2.4.13a] and [2.4.15a], and [2.4.13b] and [2.4.15b] are identical only for $n=1$. However, for $n > 1$, the model equations would give different predictions. Equations [2.4.13b] or [2.4.15b] can be used to predict the non-isothermal crystallization data once the temperature dependence of the quiescent crystallization rate constant $k(T)$ is evaluated from isothermal experiments and half-time analysis.

Dietz (77) has noted that neither of the above relations account for the effects of secondary crystallization. He proposed the following modified crystallization rate equation to account for slower secondary crystallization

$$\frac{d\theta}{dt} = n k(T) t^{n-1} (1 - \theta) \exp \left(\frac{-a\theta}{1 - \theta} \right), \quad a \geq 0 \quad [2.4.16]$$

where $\theta = X(t)/X_{\infty}$. Dietz erroneously noted the above equation to be a modification of the Nakamura model. The Dietz model is in fact a modification of a differential form of the Kamal model ($a=0$ leads to differential form of Kamal model). Although Dietz's equation may be an improvement over the Kamal model for polymers that exhibit extensive secondary crystallization, it introduces the additional parameter "a" which must be evaluated.

Some investigators have used non-linear regression methods to fit nonisothermal data directly (76,78). Using the parallel Kamal model (a dual crystallization form of equation [2.4.15]) Cebe (78) fitted the nonisothermal data for APC-2 PEEK directly. A non-linear least squares fitting routine was used to fit the data separately for nonisothermal cooling rates of 1, 5 and 10 °C/min. The strategy for fitting was to fit the initial part of the data with a single Avrami equation to narrow down the values of n_1 . Then the latter part of the data was fit with the addition of the second process, to narrow down the values of n_2 . These predetermined n -values were then fixed, and the remaining parameters C_1 , C_2 , C_3 and w , for both the processes, were allowed to vary freely to achieve the best fit. Cebe also considered how sensitive the fit was to the choice of input parameters, and whether equally good fits could be achieved with different sets of parameters. Cebe did not describe the fitting algorithm used. However, different values of the parameters were obtained for different cooling rates for the same polymer. Hence, the analysis is of little practical significance as it can not be used to predict the nonisothermal kinetics at higher cooling rates obtained in many processing operations, especially in fiber spinning.

Stress-induced crystallization : Polymer crystallization is very sensitive to molecular orientation in the amorphous regions in addition to the thermal conditions. During processing of semicrystalline polymers, crystallization almost always takes place in the presence of molecular orientation, under non-isothermal condition. The various effects observed during the crystallization of polymers in the oriented or deformed states can be divided into three groups related to thermodynamics, kinetics and morphology, respectively.

A thermodynamics description, first presented by Flory (88), was extended by Kobayashi and Nagasawa (89) and Ziabicki (90). These theories predict an increase of

the equilibrium melting temperature mainly due to the decreased entropy content of the deformed macromolecular system. On a qualitative basis this effect was confirmed with experiments performed on crosslinked rubbers (91,92).

There is direct experimental evidence that molecular orientation also strongly affects the polymer morphology. The effect consists mainly of a gradual transition from spherulitic to non-spherulitic morphology (93-96). It is known that the orientation of crystals in crystallized samples depends on the orientation of the amorphous material prior to crystallization (97-99), but the organization of polymer crystals obtained under molecular orientation is not fully understood.

Very few papers dealing directly with a quantitative evaluation of kinetic parameters for uncrosslinked polymers have been published so far. It has been demonstrated that crystallization rate increases remarkably on increasing the orientation or deformation of macromolecular chains. The effect of orientation on kinetics was first discussed by Dunning (100) in terms of crystallization kinetic theory and was later improved by other authors (89,101). The most reliable data on the kinetics of oriented crystallization concern cross-linked rubbers. Isothermal crystallization of elongated samples held in isometric conditions yield crystallization rates and Avrami exponent as a function of deformation. On the other hand crystallization experiments in shear flow, stirred systems or in elongational flow only yield indirect or qualitative information about crystallization rates and morphology of oriented crystallized material.

Katz (102) found that amorphous natural rubber would crystallize when stretched. Treloar (103) and Gent (104) observed a rapid increase in crystallization rate and decrease in Avrami exponent, reaching $n=1$ for vulcanized rubbers with increasing deformation. Kim and Mandelkern (105) found decreased value of n from 3.6 for isotropic rubber (stretch ratio $\lambda = 1$) to 1.3 for $\lambda = 6$ based on stress relaxation experiments. Observations

have been made in shear flow or in the stirred polymer solutions confirming the increase in incipient crystallization temperatures and rates (89,106,107) while induction times were found to decrease with shear rate or stirring velocity (108).

Wasiak et al. (109) studied crystallization kinetics of oriented PET in a temperature range close to T_g . They showed that orientation of the amorphous phase led to a substantial increase in crystallization rate and this effect, in turn, depended on the crystallization temperature: the higher the temperature, the stronger is the effect of orientation. Many observations concerning polymer crystallization in elongational flow are indicative of the great importance of orientation effects in fiber formation. Bai (110) observed that melt spun PET fibers are usually amorphous due to very low kinetic crystallizability, however, high speed spinning accompanied by strong molecular orientation, despite an increased cooling rate, produces partially crystalline fibers. Similar experimental observations were made by Zieminski (14) for high speed spun nylon-66 and by Bheda (17) for nylon-6. This can only be explained when one assumes that the increase in crystallization rate due to molecular orientation is so large that it more than compensates for the effect of reduced crystallization time. Dees and Spruiell (111) observed an eight fold reduction in the crystallization half time for PE fibers spun at higher take-up velocity.

Ziabicki (21) has presented a phenomenological analysis of orientation phenomena and proposed simpler and more tractable formulas for orientation dependent crystallization rates which can be directly used in the interpretation of polymer processing. He proposed that any sufficiently smooth function of molecular orientation (f), X , can be expressed as

$$X(f) = X(o) + a_2f^2 + a_3f^3 + \dots \quad [2.4.17]$$

where $X(f)$ represents any scalar-valued function of molecular deformation, e.g., melting temperature T_m , crystallization rate K , etc. The linear term from the above equation drops out for symmetry reasons. For not too high orientations, i.e. considering only the quadratic term, one can obtain

$$\ln(K(f)/k(0)) \approx A(T)f^2$$

or

[2.4.18]

$$K(T,f) = K(T,0) \exp(Af^2)$$

It is easy to see that equation [2.4.14] predicts a monotonic increase in K with increasing orientation (A is always positive). The temperature dependent parameter, $A(T)$, can be considered as an empirical characteristic to be determined. Experiments made by Wasiak et al. (109) on PET gave the value of A to be 210 at 95 °C and 940 at 115 °C.

Kobayashi and Nagasawa (89) assuming similar nucleus type in both the quiescent and the stressed case, evaluated the ratio of the stress-induced to quiescent nucleation rate:

$$\frac{N(\text{stressed})}{N(\text{quiescent})} = \exp \left[\frac{8\pi \sigma_s^2 \sigma_e}{kT} \left(\frac{1}{\Delta f_{\text{def}}^2} - \frac{1}{\Delta f^2} \right) \right] \quad [2.4.19]$$

Similar type of equation for the ratio of the oriented to unoriented growth rates was expressed by them as:

$$\frac{G \text{ (stressed)}}{G \text{ (quiescent)}} = \exp \left[- \frac{4 b_o \sigma_s \sigma_e}{kT} \left(\frac{1}{\Delta f_{\text{def}}} - \frac{1}{\Delta f} \right) \right] \quad [2.4.20]$$

where Δf_{def} is the free energy change during orientation induced crystallization, Δf is the free energy change during quiescent crystallization, which can be expressed as

$$\Delta f = \Delta H_f(\Delta T/T_m) \quad [2.4.21]$$

If it is assumed that the change in free energy of crystallization between orientation induced crystallization and quiescent crystallization is due to the entropy difference between the oriented and isotropic amorphous region, then

$$\Delta f_{\text{def}} = \Delta f + T(\Delta S - \Delta S_{\text{def}}) \quad [2.4.22]$$

where ΔS and ΔS_{def} are the entropy changes during crystallization under quiescent and oriented conditions, respectively. The theory of rubber elasticity yields (112)

$$(\Delta S - \Delta S_{\text{def}}) \propto (\lambda^2 + 2/\lambda - 3) \quad \text{and} \quad \Delta n \propto (\lambda^2 - 1/\lambda) \quad [2.4.23]$$

where λ is the extension ratio. For small extensions i.e. for $\lambda \approx 1$, $(\Delta S - \Delta S_{\text{def}}) \propto (\Delta n)^2$. Further, $\Delta n \propto f_a$.

Thus we have

$$\Delta f_{\text{def}} = \Delta f + C T f_a^2 \quad [2.4.24]$$

where f_a is the amorphous orientation factor and C is an arbitrary constant.

Combining equations [2.4.15], [2.4.16] and [2.4.19], one can derive

$$G_{\text{def}} = G \exp \left[\frac{4 b_o \sigma \sigma_e T_m}{k \Delta H_f T \Delta T} \left(1 - \frac{1}{1 + C \left(\frac{T}{\Delta T} \right) f_a^2} \right) \right] \quad [2.4.25]$$

Katayama et al. (16) and Zhou (20), assuming that the overall rate of crystallization (the Avrami rate constant) has the same form of temperature dependence as the growth rate, obtained :

$$k(T, f_a) = k \exp \left[\frac{4 b_o \sigma \sigma_e T_m}{k \Delta H_f T \Delta T} \left(1 - \frac{1}{1 + C \left(\frac{T}{\Delta T} \right) f_a^2} \right) \right] \quad [2.4.26]$$

In polymer processing, crystallization behavior is influenced by two competitive effects, viz. cooling rate and the crystallization rate. Cooling rate is controlled by the heat transfer of the polymer sample to its surroundings, i.e., the cooling medium, and the mass of the polymer. The crystallization rate is determined by polymer type and the presence of molecular orientation. As already noted, the crystallization rate is enhanced by the presence of the molecular orientation. The effect of molecular orientation can be very large, but it is difficult to measure and quantify. Spruiell and White (113) have introduced the concept of continuous cooling transformation (CCT) curves, which are well known in metallurgy and solid phase transformation literatures (114,115), to compare the kinetics of stress-induced crystallization during polymer processing to those for quiescent melts of the same polymer. This is shown in Figure 2.1.

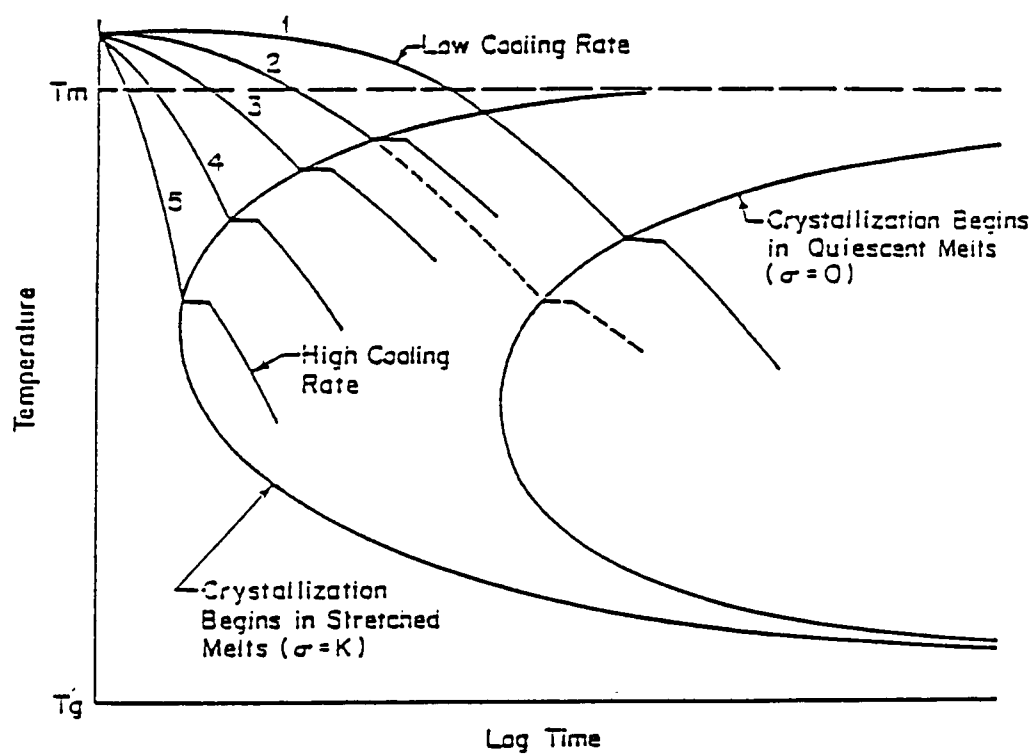


Figure 2.1. Schematic illustration of the concept of a "continuous cooling transformation curve" showing the anticipated effect of stress in shifting such curves.

2.5 Orientation and Birefringence in Flowing Melts

The development of birefringence in flowing polymer solutions was first noted by Maxwell (116) in 1873. At temperatures well above the glass transition temperature polymers are considered to be in thermodynamic equilibrium with external stresses. This means that no residual stresses are possible. If the true tensile stress $\Delta\sigma = \sigma_I - \sigma_{II}$ ($= \sigma_{11} - \sigma_{22}$ in case of melt spinning) is not too high (probably less than 10^6 Pa), one observes a linear relation between the observed birefringence and the difference between the principal stresses, known as the stress-optical law:

$$\Delta n = C_{op} \Delta\sigma \quad [2.5.1]$$

where $\Delta n = n_I - n_{II}$ ($= n_{11} - n_{22}$ in case of melt spinning) is the difference of principal refractive indices between the directions of the stretch and perpendicular to it, and C_{op} is the stress-optical coefficient. An expression, relating C_{op} to the optical anisotropy of the chain molecules is borrowed from the theory of ideal rubbers (112,117). It reads:

$$C_{op} = \frac{2\pi}{45 kT} \frac{(n^2 + 2)^2}{n} (\alpha_1 - \alpha_2) \quad [2.5.2]$$

where n is the average refractive index of the material and $(\alpha_1 - \alpha_2)$ is the difference of polarizabilities of the random link in Kuhn's model. If the polarizability along the chain is greater than that perpendicular to the chain, C_{op} will be positive. If the polarizability perpendicular to the chain is greater, C_{op} should be negative. It should be noted that the coefficient, C_{op} , is inversely proportional to absolute temperature (other than included in the temperature dependence of $(\alpha_1 - \alpha_2)$, the segment anisotropy). The above theory only

applies in the rubbery state where the stress arises from the change in entropy with elongation. This is not true in the glassy state where the enthalpy changes and there is a "distortional birefringence".

Matsumoto and Bogue (118) showed that Eq. [2.5.1] is valid for polystyrene melts under nonisothermal conditions. They also noted that the linearity of Eq. [2.5.1] is only valid at low stresses. Deviations towards lower birefringence were found at stresses of 5×10^6 Pa.

2.6 Structure Development in Fiber Spinning

Spinning conditions affect not only the degree of crystallinity but also other parameters of crystalline texture. In polymers capable of forming various structural modifications, the structures formed during melt-spinning may differ from those obtained by slow crystallization in bulk or formed in the drawing process. For example, undrawn nylon-6 fibers spun at high speeds exhibit a nearly hexagonal, γ , modification (119), while heat treatment and/or cold drawing leads to the monoclinic, α , crystal structure (120). Hexagonal crystallites in nylon-6 fibers are usually oriented with c-axes (those parallel to molecular chains) along the fiber axis (120). The degree of crystallite orientation was found to increase with spinning velocity and to decrease with filament thickness. Ziabicki and Kedzierska (121,122) were among the earliest to make basic studies of structure development during melt spinning of nylon-6. They obtained WAXS patterns and measured birefringence of spun fibers. The birefringence was found to be an increasing function of spinline stresses. In isotactic polypropylene, undrawn fibers contain monoclinic and "smectic" modifications in amounts dependent on spinning conditions. The smectic modification prevails in the conditions of rapid quenching (e.g., in a cold water bath) (123) and in spinning from high temperature melts (123,124). The

proportion of both structural forms in polypropylene fibers was found to be very important for the drawing process and the ultimate structure of drawn and heat-treated fibers (124). The orientation pattern can be quite complex in polyolefin fibers as shown by the dynamic structural studies of Katayama et al. (125) on polyethylenes and isotactic polypropylenes. Various types of crystallite orientation were found in isotactic polypropylene fibers (125). First to be formed are crystallites with c-axis orientation, and then appear also crystallites oriented with a*-axis along the spinning direction. It was found that the latter are less stable and melt more easily than c-axis crystallites. Independent determination of two orientation factors f_c and f_a combined with the condition of orthogonality ($f_a + f_b + f_c = 0$) yields detailed information about the orientation of principal crystal axes in melt-spun fibers.

All these results show that orientation conditions preceding and accompanying crystallization affect not only crystallization rates but also the type of crystal orientation. Similar observations concerning crystallization of oriented glassy PET were due to Wasiak (109). Dees and Spruiell (111) discussed three morphological forms of crystallized polyethylene explaining various types of crystal orientation: spherulitic (very low take-up speeds, no crystal orientation); row-nucleated twisted lamellae (low take-up speeds), and row-nucleated untwisted lamellae (medium to high speeds, C-orientation). The work of Nadella et al. (126) showed that both structural characteristics and mechanical properties of polypropylene filaments can be correlated with the stress in the spinline at the point of crystallization. The effects of changing such parameters as extrusion temperature or polymer molecular weight could be traced to their effects on the spinline stress.

More recently, many studies have been published describing the effect of high spinning speeds on the structure and properties of various fiber forming polymers. In

recent years the spinning speeds of PET fiber have increased to the point that significant structure development is being observed in the spun yarn. Heuvel and Huisman (127) have characterized as spun PET (0.63 IV) yarns produced at speeds up to 6000 m/min. On the basis of density measurements, they found the onset of crystallization to occur between 3500 and 4000 m/min. An interesting observation on the 4750 to 6000 m/min samples was that the crystalline density based on X-ray determination of unit cell dimensions increased with speed (1.448 g/cc to 1.501 g/cc and the estimated crystallization temperature also increased (186 °C to 218 °C). The DTA traces for these yarns confirm the structure change in the region of 3500 to 4500 m/min.

Shimizu et al (128-130) in a series of papers have studied the spinning of PET at speeds up to 7500 m/min. In the first paper (128) the properties of as spun (0.644 IV) PET are discussed and are generally in accord with the results of Heuvel and Huisman (127). Density, X-ray, tensile, DTA and shrinkage data indicate the onset of the crystallization process occurring in the 3500-4500 m/min range. These authors report significantly higher crystallinity than Heuvel and Huisman, e.g., 40 percent versus 24 percent at 6000 m/min and somewhat lower crystalline orientation factor e.g., 0.91 versus 0.98 at 6000 m/min. Shimizu et al. (129,130) have also examined the effects of flow rate per hole and the molecular weight as measured by IV over the speed range.

Lu and Spruiell (131) studied the fine structure and tensile mechanical properties of high speed spun filaments prepared from three polypropylenes with melt flow indices in the range 12-300. They found that spinnability and the resulting structure and properties are affected by both the weight average molecular weight and the polydispersity of the polymer. From on-line measurements, they also found that the crystallization onset temperature varied considerably with change in take-up velocity, extrusion temperature and resin melt index. They attributed the observed behavior to the

role of spinline stress in producing molecular orientation and consequent increase of crystallization rate. Bheda and Spruiell (18) have studied the effects of throughput rate and the molecular weight as measured by IV on structure development in nylon-6.

2.7 Mathematical Modeling of Fiber-Spinning

Although seemingly simple, the melt spinning process contains many variables which interact with one another and make a complete understanding of it quite difficult. The primary independent process variables include 1) the mass flow rate of the polymer melt, 2) the take-up velocity of the wound-up filaments, 3) the extrusion temperature, 4) the spinneret orifice shape and dimensions, 5) the spinline length, and 6) the cooling conditions along the spinline. In addition, a multitude of resin characteristics interact with the process variables to influence the processing-structure-properties relationships of the spun filaments. The major features of these effects are associated with melt viscoelasticity and crystallizability and/or crystallization kinetics. The major features of these effects are associated with melt viscoelasticity (controlled by resin molecular weight and its distribution) and crystallizability and/or crystallization kinetics. Because of the large number of interacting variables that affect the melt spinning process, a mathematical model of the process is quite valuable for developing an understanding of the process.

As in any model of a physical system, some assumptions must be made in order to develop a usable set of equations. In the case of fiber spinning, the assumption of uniform axial velocity and temperature over a cross-section as well as steady state assumption lead to a system of first order ordinary differential equations. The axial conduction along the filament and viscous heating is usually neglected in the energy balance. These assumptions (13) are usually made to make the mathematical model more tractable.

In melt spinning of slowly crystallizing polymers such as PET, there are three speed regimes that can be defined in the context of a phenomenological model:

- (a) Low-speed $V_L < 750$ m/min - The spinline tension is constant along its entire length.
- (b) Intermediate-speed $750 < V_L < 3500$ m/min - Spin-line tension varies along its length due to the effects of gravity, inertia and aerodynamic drag.
- (c) High-speed $V_L > 3500$ m/min - Spin-line tension varies along its length, as above, but is dominated by the structural changes, i.e., crystallization, that begin to occur during spinning.

The first attempt to model the melt spinning process was made by Kase and Matsuo (5-7). They analyzed the low-speed spinning process, in which they neglected the effects of gravity, inertia and air drag (hence, $F_{rheo} = F_{ext}$) and assumed Newtonian behavior. For heat transfer they assumed a forced convection mechanism, with the effect of cross flow included (radiation was neglected). Note that, while tension is assumed constant, the stress increases down the spinline due to the monotonically decreasing cross-sectional area. They show that spun yarn birefringence correlates well with the calculated spinline stress at the point where the velocity has reached 95 percent of its final value (the godet roll speed).

Hamana et al. (132) extended Kase and Matsuo's model by including air drag, gravity and inertial force terms in the balance equation and applied their analysis to PET and nylon 6 assuming Newtonian behavior. They operated mainly in the low-speed regime, the maximum velocity being 900 m/min for PET.

George (4) applied the model of steady state melt spinning at intermediate take-up speeds for PET. The model precluded the crystallization and hence has as an upper bound the speed at which stress induced crystallization begins to occur in the spinline.

The calculated temperature and velocity profiles were shown to agree with the measured value. The stress at the freeze point was found to correlate well with the spun yarn birefringence.

The models described so far did not include crystallization in the spinline and were applied to amorphous polymers or to slowly crystallizing polymers spun at speeds where no crystallization takes place in the spinline. Recently, Katayama and Yoon (16), Shimizu et al. (15), Vassilatos et al. (133) and Zieminski and Spruiell (13) have developed models that include the effects of crystallization. These models have been applied to high speed spinning of PET, nylon-66, nylon-6 as well as to low to medium speed spinning of fast crystallizing polymers such as LDPE, LLDPE and polypropylenes.

The model developed by Zieminski and Spruiell (13) included effects of acceleration, gravity and air drag in the force balance equation and the effects of temperature and molecular orientation on the crystallization kinetics of the polymer based on the empirical approach by Ziabicki (21). The model also included the effect of crystallinity on the elongational viscosity of the polymer as proposed by Kikutani (134). The model used the Newtonian constitutive assumption to predict kinematic response of polymer melt in the spinline. They found a good agreement between online experimental measurements (diameter, temperature and birefringence profiles) for nylon-66 and those of Lu and Spruiell (131) on polypropylenes with the model predictions. However, in both the cases online diameter data were restricted to the mostly solidified region of the spinline. Zieminski and Spruiell (13) concluded that orientation induced crystallization occurred in nylon-66 for spinning speeds greater than 4000 m/min and it was relatively insensitive to variation in Avrami exponent in the range of 1 to 3 and to the variation of exponent of crystallinity in elongational viscosity expression in the range from 2 to 12.

There are very few reported rigorous attempts at using viscoelastic constitutive

equations for mathematical simulation of non-isothermal fiber spinning (135,136,35,10). Matsui and Bogue (35) have used the integral formulation to predict stresses in slow speed nonisothermal spinning using experimental velocity profiles. Fisher and Denn (135) have studied the mechanics of nonisothermal polymer melt spinning using a convected Maxwell model. Denn and Gagon (10) have used a convected Maxwell model and the Phan-Thein and Tanner model, both in differential form, in their simulation of non-isothermal fiber spinning. They also compared their results with the predictions using a Newtonian constitutive equation as well as experimental data. Their simulation of PET spinning demonstrate that small variations in the heat transfer coefficient correlation can result in large changes in the predicted drawdown, and that the absence of viscoelasticity in the spinning model can be compensated for by use of a smaller heat transfer coefficient.

Historically, models have been used to calculate velocity, temperature and stress profile from the process conditions with literature values of extensional viscosity and heat transfer coefficient relations. However, analogous to isothermal spinning experiments, the apparent elongational viscosity of the resin can be evaluated from the on-line measurements made on the running non-isothermal spinline. Similarly, from the gradient of temperature profile, the heat transfer coefficient can be calculated. The required data are measurements of filament diameter and temperature as a function of distance from the spinneret coupled with a measurement of the spinline tension carried out at a position near the filament take-up device. The procedure is described by George and Deeg (19).

The diameter profile needs to be differentiated to obtain elongation rate and hence, the apparent elongational viscosity data along the spinline. In most cases, the diameter profile is smoothed either using a functional form or using polynomial or spline type fitting procedure. In a case of isothermal spinning the theory extended by Patel and

Bogue (33) gives the governing closed form solution; the generalized form of which can be used to smooth the diameter data using a non-linear regression procedure. Patel and Bogue (33) obtained identical results using the functional form based on the Newtonian theory and using $(1/D)$ versus distance polynomial for their isothermal gravity spinning data. However, the Newtonian theory in non-isothermal case does not give closed form analytical solution. Hence, various empirical fitting forms or various polynomial fitting procedures have been used to smooth diameter profile data obtained in non-isothermal spinning. George and Deeg (19) have used polynomial fitting of $\log(V)$ versus $\log(z)$ data. Bheda (17,18) used polynomial fitting of diameter versus distance data. The fitted diameter profile can be differentiated to obtain the elongation rate profile. The stress profile along the spinline is computed from the force balance and a single tension measurement towards the end of the spinline. The required calculation is the integration of the differential force balance equation [2.1.4]. The ratio of stress to elongation rate at a point on the spinline would give the apparent elongational viscosity. The computed apparent elongational viscosity data is then correlated to measured temperature profile to obtain the rheological spinning function (RSF). The differentiation of the temperature profile would give heat transfer coefficient data and a thermal spinning function (TSF). The rheological spinning function (RSF) is essentially the apparent elongational viscosity as a function of temperature which can be of Arrhenius form and the thermal spinning function is the heat transfer coefficient correlation.

From the heat transfer coefficient correlation developed by Kase and Matsuo (6,7), Bheda (17) used a relation of the form

$$h = a (Vel/Area)^b \quad [2.7.1]$$

to correlate the heat transfer coefficient data. The constants a and b are evaluated from the regression analysis.

This "inversion" procedure can be best applied in the absence of crystallization occurring in the spinline or to the portion of the profile that is in the molten state. For example, in the case of nylon-6 and PET crystallization does not occur on the spinline at spinning speeds below about 4000 m/min. Hence, in such cases, one can apply this procedure to on-line data for lower spinning speeds. The RSF and TSF data obtained at a single low speed can be used to predict the spinline dynamics at higher spinning speeds.

A melt spinning process involves a large number of interacting variables. Hence, a mathematical model of the process is quite valuable for developing an understanding of the process. Appropriate assumptions, described in detail by Zieminski and Spruiell (13) are used to reduce the equations of continuity, momentum and energy balance by averaging over a filament cross-section to a set of simultaneous first order ordinary differential equations. These so-called "thin filament" equations (refer Equations [2.1.3], [2.1.4] and [2.3.1]) form the working relationships of the model. The mechanics of fiber spinning are almost always described by "thin filament" equations; the principal assumption in these equations is a small rate of change of filament diameter with distance from the spinneret, and they are clearly inapplicable at the spinneret, where curvature may be substantial. The equations are also obtained from the macroscopic balances in which it is assumed that axial velocity and temperature are uniform over a cross-section, and the flow is locally a uniform, uniaxial extension.

The solution of these simultaneous differential equations requires the specification of necessary initial and boundary conditions. Fluid emerging from the spinneret is in the midst of a transition from the shear flow in the spinneret to the elongational flow downstream. There may be extrudate swell. Consistency with the thin filament

equations requires that the origin of the axial coordinate be taken at a point where conditions are radially uniform; the finite-element calculations indicate that this point is one-to-two diameters downstream of the spinneret. Nevertheless, the initial temperature is always taken to be the extrusion temperature. The flow rate will generally be given, but the initial area is unknown because of the extrudate swell and uncertainty as to the precise location of the coordinate origin. Hence, it is customary to specify the velocity and area at $z=0$. These discrepancies should be negligible in a typical long non-isothermal spinline. Since the take-up velocity can be fixed mechanically, it is specified as one of the boundary conditions.

The momentum equation is usually expressed in terms of the rheological force on the filament. However, the force at $z=0$ is unknown and for a fixed throughput rate, the take-up velocity and the force at $z=0$ cannot be specified simultaneously for physical reasons. This observation forms the basis for iterative schemes. Specifying the force at $z=0$ converts the boundary value problem to an initial value problem. For an inelastic liquid, this is equivalent to assuming the derivative dV/dz at $z=0$. The force is then adjusted until the take-up velocity condition is satisfied. The velocity-force function is monotonic, so any elementary iterative scheme is adequate.

The boundary conditions discussed so far are sufficient for an inelastic liquid. However, an additional bit of information, the ratio T_{xx}/T_{zz} at $z=0$, is required for a viscoelastic simulation. This ratio is -0.5 over the entire filament for an inelastic fluid. The solution to the thin filament equations is insensitive to this initial stress ratio (32,33) as long as it is in the range from -0.5 to 0. The ratio is usually taken to be zero at $z=0$ in a viscoelastic simulation. The general memory integral formulations, as discussed earlier, lead to problems in the specification of the flow upstream of the spinneret. The kinematical assumptions leading to thin filament equations are also not valid for that

portion of the history prior to the spinneret exit. Hence, the differential formulation, which avoids most of the above mentioned problems, is usually used in the spinline viscoelastic simulations.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 Materials

The main objective of this research was to obtain better dynamic analysis of the non-isothermal spinline using a best possible description of spinline rheological and crystallization behavior. The spinline data obtained by Bheda (17,18) on two nylon-6 resins were analyzed using the improved process model to test its validity for nylon 6 melt spinning. One resin called CN 9984 had an intrinsic viscosity of 0.905 dl/g and a viscosity average molecular weight of 25,250, while the second resin called BHS (supplied by Allied Fibers) had an intrinsic viscosity of 1.525 dl/g and a molecular weight of 53,210. The other objective of this research was to do basic rheological, crystallization kinetics and melt spinning studies of various nylon 6 resins supplied by Allied Fibers. Three different batches of another nylon 6 resin called MBM and a batch of a nylon 6 resin called LSB were also supplied by Allied Fibers. The GPC data on various nylon 6 resins provided by Allied Fibers are shown in Table 1. BHS and one batch of MBM resin were studied extensively under quiescent isothermal and nonisothermal crystallization. All the nylon 6 resins supplied by Allied Fibers were studied using basic rheological characterization at different temperatures using mainly a cone-and-plate rheometer and also using a capillary rheometer. The first batch of MBM resin (designated as MBM-I) was found to be contaminated and was subsequently discarded. BHS, LSB and other two batches of MBM resin (designated as MBM-II and MBM-III) were studied extensively under melt-spinning using on-spinline measurements. The objective of the spinning experiments was to obtain apparent spinline elongational

Table 1. The GPC data of various Allied nylon 6 resins.

Sample	FAV	M_n	M_w
BHS	78.9	18,000	38,600
LSB	64.9	15,600	33,900
MBM-II	52.0	14,000	30,600

viscosity data of BHS, LSB, and MBM resins. The heat transfer coefficients were also obtained from on-spline temperature measurements using an improved infrared thermal imaging system and analysis. These data were then used in the simulation of Allied melt spinning processes using the improved melt spinning model.

3.2 Experimental Procedures

Melt Spinning

Fourne extruder-spinning equipment (shown schematically in Figure 3.1) supplied by Fourne Associates, Germany was used to melt spin the polymers mentioned above. The Fourne extruder had a single screw of 13 mm diameter and 300 mm length. The extruder was equipped with a seven liter capacity, nitrogen purged hopper. It had two independently controlled band-type heaters along its barrel. The spinning head also had two independently controlled band heaters similar to those on the barrel. The extruder screw received polymer chips by gravity feed from the hopper. Just underneath the hopper, the barrel throat was fitted with a cooling water sleeve to facilitate feeding of the polymer pellets from the hopper and prevent the polymer from immediate contact with the hot barrel. The screw delivered molten polymer at a pressure of 1.0×10^3 to 3.0×10^3 psi to a Zenith gear pump which maintained a constant mass flow rate through the spinneret. The gear pump speed was manually adjusted to obtain the desired mass flow rate of the polymer melt. The melt pressure was indicated by a Dyanisco pressure gauge. Molten polymer from the gear pump is passed through a 325 mesh filter screen and through a single capillary die of diameter 1.0 mm. The extruder and spinning head block is mounted on a vertical steel column which allowed the spinline length to be easily changed. An air jet drawdown device supplied by Rhone-Poulenc Fibers was used to draw down and take-up the filaments. With air pressure up to about 100 psi, this device

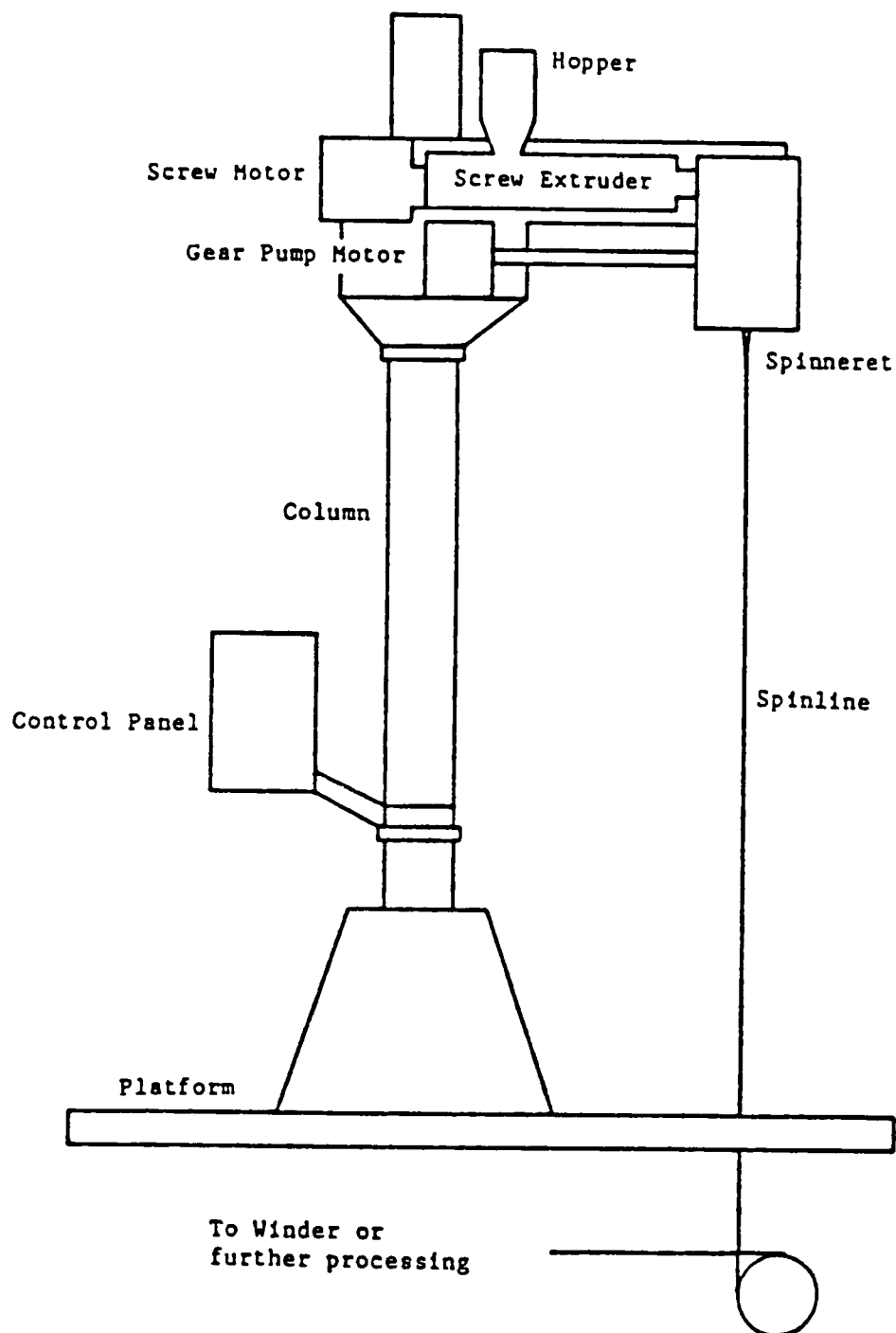


Figure 3.1. Schematic diagram of the spinning equipment.

was capable of producing take-up velocities up to about 7500 m/min. Optimum operating parameters for each resin were decided by trial runs.

Melt Spinning Procedure: Since nylon 6 absorbs moisture from air, these samples were always dried before melt spinning in a vacuum oven supplied by National Appliance Company, Portland, Oregon. The drying was carried out under near vacuum at a temperature of about 90 °C for about sixteen hours.

Several trial and error spinning runs were carried out to determine appropriate processing parameters such as temperatures of the four heating zones, screw speed, gear pump speed for controlling mass throughput rate, take-up velocity range, etc. The melt spinning began with turning on the power to the four band heaters. The first three zone temperatures were set at 240 °C, 250 °C and 260 °C, respectively. The band heater temperature for the spinneret die was set at 255 °C. It usually took about one hour for the zone temperatures to stabilize. The hopper was then loaded with the dried resin and purged with nitrogen. Before starting the extruder, a check was made to make sure that the screw could be rotated freely. The gear pump motor was turned on first, followed by the screw motor. The screw speed was gradually increased until the melt pressure before the gear pump was in the range of 1000-2000 psi. After stabilization of the melt pressure, the mass throughput (g/min) was measured by collecting the extruded polymer for a minute and weighing the output on a balance. The gear pump speed was adjusted to obtain a desired mass throughput rate. The machine was then run for about 45 minutes before starting on-line measurements. The temperature display panel on the extruder showed the die-zone temperature of about 270 °C. The temperature of the spinneret die with molten polymer inside, measured using a calibrated thermocouple, was found to be about 245 °C. The spinneret diameter was 1000 micrometers.

The air-jet drawdown device had no direct indication of take-up speed. However, the take-up velocity could be varied by varying the pressure of the compressed air supplied to the device. The pressure gauge at the aspirator gave the pressure reading of the compressed air supply. The final take-up velocity was calculated using the continuity equation through final fiber diameter and density measurements.

On-line Measurements

On-line non-contact experimental measurements of diameter, temperature, birefringence and x-ray patterns provide a direct means for developing an understanding of the dynamics and structure development during melt spinning. In addition to following the development of molecular orientation and locating the position and temperature of crystallization in the spinline, such data are quite useful for comparison with the predictions of mathematical models of the melt spinning process.

Diameter measurements: The on-line diameter measurement was carried out using a Zimmer system (Diameter monitor model 460A/2 and Digital Controller model 466/2) supplied by Zimmer OHG, Germany. The instrument is based on a non-contact electro-optic back illumination principle permitting measurements on both opaque and semi-transparent materials. The Zimmer diameter monitor has a range of 0 to 2 mm for diameter measurement with a resolution of 0.5 micrometers. It is to be noted that the displayed diameter is a reading averaged over 11 mm of filament length. An IBM-AT personal computer was interfaced with the Zimmer system to collect and store data. Two thousand diameter values were collected by the computer at each position. Since the nylon 6 filaments were semitransparent, the diameter data were corrected for transparency. The measured diameter data showed substantial variation, due to movement of the fiber in and out of focus field of the sensor and to variations in

throughput rate and take-up tension due to air suction force. A statistical computer program, written by Steve Steiner of the electronics shop, was used to compute average diameter value at each position.

In actual experiments the Zimmer monitor was mounted on a movable carriage so that the sensor could be moved up and down the spinline. Before measurement it was required to zero the instrument and calibrate it. The calibration was done by inserting a Zimmer calibration standard, an opaque metal wire of 100 micron diameter. The measurement started near the bottom position of the spinline close to the take-up device, and moved up at 10 centimeter interval until reaching 10 centimeters from the spinneret. After every measurement, the running filament was moved out of focus field of Zimmer to check the zero of the instrument. It was found that the Zimmer monitor was not returning to zero value, especially near the spinneret. Hence, it was necessary to zero the monitor after each measurement. Near the spinneret, the Zimmer monitor was shielded by a thick phenolic insulating plate.

Temperature measurement: The online temperature profiles were measured using a Hughes PROBEYE 3300 InfraRed thermal imaging system. According to the manufacture's literature, the system can measure temperature from -20 °C to 950 °C and it is sensitive to radiation in the spectral range from 2 to 5.6 microns. The system does not measure temperature directly. Instead, it measures the radiant power received by the infrared camera. If the emissivity of the surface is not known, the radiant power measured by the instrument can not be related to the temperature of the emitting surface. Accordingly, the detector displays the temperature at which a black body would emit the same radiant power. This temperature is referred to as the apparent black body temperature. The term apparent is used here because the power received by the instrument is not solely emitted by the surface. Instead, the received power includes also

the radiation coming from the surroundings which is partially reflected and transmitted by the surface before it reaches the instrument. The online temperatures were first measured in terms of the apparent black body temperature. Vibrations of the running spinline leads to filament getting in and out of the focus of the thermal imaging camera. The instrument can capture a thermal image of the running filament, which was then analyzed to obtain the apparent black body temperature of the filament (which is the maximum black body temperature across the cross-section of the filament). Because of the vibrations of the running spinline, it is essential to capture the thermal image of the filament when it is in focus. In order to convert the apparent black body temperature into actual temperature, the emissivity of the fibers must be known at each position of the spinline where measurements were collected. The emissivity of the filaments were measured by Hajji (137) as a function of diameter and temperature of filament using independent experiments. Hajji (137) has shown that the emissivity of nylon 6 depends only on the diameter of the filament. The actual temperatures along the spinline were then obtained by applying the emissivity correction. .

Birefringence measurement: On-line birefringence of the running filament for BHS and CN 9984 resins was measured by Bheda using an Olympus polarizing microscope (model 206080) and an olympus 4 order berek compensator (model CTPI-200205) to measure the optical retardation. The microscope was mounted on a movable stand which can be moved up and down and around. The microscope was set at an appropriate position and angle to the spinline. The filament was guided within the microscope's viewpoint using a v-groove arc type aluminum guide.

The measurement was made with crossed polars on the microscope. At the zero reading on the compensator a black band was observed across the field of view. When a

birefringent fiber was brought into view the black band was shifted and the optical crystal of the compensator was tilted until the black band was brought back to zero reference position. The retardation was calculated from the compensator reading and the birefringence was calculated by dividing the retardation by the fiber diameter.

Tension measurement: The tension in the spinline was measured using a Rothschild Tensiometer model INTEG R-1198 measuring head with computer-aided data acquisition. The instrument was calibrated using 100mg, 200mg, 300 mg, 500mg, 1g, and 2g dead weights attached to a filament. The filament was pulled slowly through the tensiometer head by a variable speed electric motor.

Before on-line measurement, the instrument was zeroed. The tension near the bottom of the spinline was measured by carefully inserting the measuring head into the spinline. There was a consistent problem of filament sticking to the tensiometer head and subsequent breakage of spinline. Anti-stick spray was frequently necessary to avoid sticking. For a given measurement, 2000 readings were collected by the computer and an average value of tension was calculated using a statistical program.

Rheological Measurements

The basic rheological data (the shear viscosity and the first normal stress difference) at various temperatures for the various nylon 6 resins were obtained at low shear rates using a cone-and-plate rheometer (Rheometrics Mechanical Spectrometer). The compression molded plates from dried resin were prepared using a melt press equipment. The plates were compression molded at about 240 °C and rapidly cooled by running water tubes in the platens of the compression molding set-up. Air bubble free portions of the plate were cut into 1"x1" plates using a printed circuit board (PCB) cutter. These 1"x1" plate samples were used in the Rheometrics cone-and-plate rheometer. The

cone had a 25 mm diameter with 0.1 radian cone angle. The shear stress and the first normal stress difference are determined by measuring the torque (τ) and the thrust (F). The equations to obtain the shear stress and the first normal stress difference at various shear rates are given elsewhere (32). The shear viscosity data at various temperatures for the various nylon 6 resins were obtained at high shear rates using an Instron Capillary viscometer. The capillary die had a diameter of 0.04" and $(L/D)=35$ and 50. The appropriate equations for computing viscous properties of fluids in a capillary viscometer using Rabinowitsh correction are given elsewhere (32).

Quiescent Crystallization Kinetics Measurements

Both isothermal and nonisothermal crystallization kinetics of BHS and MBM-I resins were studied using a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples for crystallization kinetics were prepared as films using dried resins. The films of MBM-I resin were prepared after removing pellets of unknown polymer. The sample weights ranged from 6-9 mg. The DSC-7 calorimeter was calibrated for temperature according to the procedure described in the user's manual using pure indium as standard ($T_m=156.6$ °C). The isothermal crystallization was studied in the temperature range of 180-200 °C. Below 180 °C, the crystallization was too rapid to follow accurately. A Mettler FP 82 hot stage was used to melt the samples at 270 °C for at least 5 minutes. Each melting was followed by a rapid transfer to the DSC chamber maintained at the desired crystallization temperature. All isothermal crystallizations were carried out under the flow of dry nitrogen to reduce the chances of thermal degradation. The resulting crystallization isotherms were rescaled and plotted using an HP 7470A plotter attached to the DSC. These plots were digitized by a Tektronics 4594 digitizing tablet, and the data were transferred to an IBM-PC for analysis. Such data were fitted with a cubic spline interpolating procedure and integrated using FORTRAN subroutines. A linear baseline

between the onset and the end of crystallization was assumed. The relative crystallinity which developed up to time t was determined from the heat released by crystallization as a function of time t by the following equation:

$$\frac{X(t)}{X_{\infty}} = \frac{\int_0^t \left(\frac{dH}{dt} \right) dt}{\int_0^{\infty} \left(\frac{dH}{dt} \right) dt} \quad [3.2.1]$$

where dH/dt is heat flow rate.

The nonisothermal crystallization was carried out at constant cooling rate of 2, 5, 10, 20 and 40 °C/min. Again, samples were kept at 270 °C for at least 5 minutes before cooling at a constant cooling rate. The relative crystallinity which developed on cooling to temperature T was again defined to be the fractional area confined between the rate-time curve and the baseline. The DSC data were again digitized and cubic spline interpolation was used to calculate area under the curve using FORTRAN subroutines. The temperatures were corrected for a small thermal lag between the sample and the calorimeter furnace using a relation developed by Hammami (80).

CHAPTER 4

DEVELOPMENT AND DESCRIPTION OF MELT SPINNING MODELING PROGRAM

This chapter gives the details of the Newtonian melt spinning program development. The spinline model developed by Zieminski (13,14) using CSMP package on the IBM mainframe and subsequently used by Bheda (17) and other researchers at the University of Tennessee was improved, simplified and implemented on the IBM PC. Major simplifications involved 1) use of drag coefficient correlation in terms of air Reynolds number instead of Sakiadis (23) approach, 2) use of a differential form of Nakamura model (refer to Equation [2.4.14]) instead of the integro-differential form of the Nakamura model used by Zieminski (13,14) to evaluate spinline crystallization kinetics, 3) use of a single overall differential force balance equation instead of treating individual force components separately, 4) use of linear stress-optical law to compute birefringence instead of stress-optical relation involving a time constant. These major simplifications made the spinline model equations more tractable. The improved spinline model also assumed Newtonian rheological behavior. In the present version, the model ignores radial variations in the filament, heat conduction along the spinline, viscous heating and the surface tension of the polymer/air interface. Application of the kinematics of melt spinning, together with these assumptions and the above mentioned simplifications, to the equations of continuity, momentum and energy balance led to a set of working relationships for the model.

A summary of the relationships used in the improved model is shown in Figure 4.1. The model differential equations consist of four simultaneous first order ordinary differential equations, one each for force balance, rheological constitutive equation,

1. CONTINUITY

$$W = (\pi D^2/4) \rho V$$

$$V(0) = V_0 \text{ with } D(0) = D_0$$

2. MOMENTUM BALANCE

$$dF_{rheo}/dz = W \, dV/dz + 1/2 \, \rho_a \, C_d \, V^2 \, \pi D - W \, g/V$$

$$F_{rheo}(0) = ? \text{ (Guess); } C_d = k \, Re^{-n}$$

3. ENERGY BALANCE

$$\frac{dT}{dz} = - \frac{\pi D h (T - T_a)}{W C_p} + \frac{\Delta H_f}{C_p} \frac{dX}{dz}$$

$$T(0) = T_0$$

4. RHEOLOGICAL CONSTITUTIVE EQUATION

$$\sigma = F_{rheo}/(\pi D^2/4)$$

$$\frac{dV}{dz} = \frac{\sigma}{\eta(T)}; \quad \eta(T) = A \exp\left[\frac{B}{T+273}\right] \exp\left[a\left(\frac{X}{X_\infty}\right)^b\right]$$

5. BIREFRINGENCE AND ORIENTATION

$$\Delta n_a = C_{op} \, \sigma \quad f_a = \Delta n_a / \Delta a^0$$

$$\Delta n = (1-\theta) \Delta n_a + \theta f_c \Delta c^0$$

6. CRYSTALLIZATION KINETICS

$$\frac{d\theta}{dz} = \frac{nK}{V} (1-\theta) \left[\ln\left(\frac{1}{1-\theta}\right) \right]^{\frac{n-1}{n}} \quad \text{where } \theta = \frac{X(t)}{X_\infty}$$

$$\theta(0) = 0$$

$$K(T, f_a) = (\ln 2)^{\frac{1}{n}} \left(\frac{1}{t_{1/2}} \right)_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{C_3}{T \Delta T + C T_a^2 f_a^2}\right]$$

OR

$$K(T, f_a) = K_{max} \exp\left[-4 \ln(2) \frac{(T - T_{max})^2}{D^2} + C f_a^2\right]$$

Figure 4.1. Summary of the working relationships of the improved fiber spinning model.

energy balance and crystallization kinetics. These differential equations need to be solved to obtain stress, velocity, temperature and crystallinity profile along the spinline. The diameter profile can be calculated from the velocity and temperature profiles using the equation of continuity. From the stress profile, amorphous birefringence along the spinline then can be calculated using the stress-optical law. The crystalline birefringence can be calculated from crystallinity profile and assuming the crystalline orientation factor. The total birefringence along the spinline can be calculated by adding amorphous and crystalline birefringence. The elongation rate profile can be obtained from stress, temperature and crystallinity profile using rheological constitutive equation. Note that the spinline elongational viscosity under Newtonian assumption depends on temperature as well as crystallinity. This set of simultaneous first order differential equations was solved using a fourth order Runge-Kutta method using a BASIC program written by the author for an IBM PC. The IBM Advanced BASIC interpreter was used while writing the program. The spinline modeling program was executed with a BASIC compiler called TURBOBASIC supplied by Borland international, Inc. The compiler is compatible with IBM Advanced BASIC (commonly referred to as BASICA) interpreter and it uses the 8087 math coprocessor for faster execution. The melt spinning modeling program can also be executed using Microsoft QBASIC compiler.

For a melt spinning simulation, the process variables to be specified are 1) W in g/min, 2) die diameter in cm, 3) melt temperature at the die in $^{\circ}\text{C}$, 4) length of the spinline in cm, 5) take-up velocity in m/min, and 6) the cooling conditions: quench air velocity in cm/s and temperature in $^{\circ}\text{C}$ (or stationary ambient air temperature). Apart from the above process conditions, correlations for heat transfer coefficient need to be obtained for given cooling conditions. The resin variables to be specified are the apparent elongational viscosity data as a function of temperature and the resin crystallization

kinetics data.

In addition, correlations are required for melt specific heat capacity (C_p), melt density (ρ_m), air density, and air viscosity as a function of temperature. Finally, the values of stress optical coefficient and intrinsic birefringence (both amorphous and crystalline) for nylon 6 are needed in the program.

The variables used in the IBM PC source code for modeling of a single filament spinline (circular spinneret) written by the author are listed below. All the variables are in CGS units.

Frheo	= Rheological force in the filament, dynes.
XOP	= Temperature of the filament, °C.
CRYST	= Percent crystallinity.
UCRYST	= Ultimate crystallinity.
KK	= Crystallization rate, sec ^{-NN} .
NN	= Avrami index.
CC	= Stress-induced crystallization parameter.
FC	= Crystalline orientation factor.
TBIR	= Total birefringence.
ABIR	= Amorphous birefringence.
AOF	= Amorphous orientation factor.
W	= Mass throughput rate, g/min.
DIA	= Diameter of the filament, cm.
U	= Velocity of the filament, cm/s.
DU	= Elongation rate, sec ⁻¹ .
RM	= Density of nylon, g/cm ³ .
SIGMA	= Stress in the filament, dynes/cm ² .
NEAPP	= Apparent elongational viscosity, Poise.
HTC	= Heat Transfer coefficient, Cal/s/cm ² /°C.
QAV	= Quench air velocity, CM/sec.

TA = Ambient air (or quench air) temperature, °C.
 RA = Air density, g/cm³.
 MUA = Viscosity of air, Poise.
 H = Increment length.
 CD = Air drag coefficient.
 CP = Specific heat capacity, Cal/g/°C.
 GR = Acceleration due to gravity, dynes/gm.

The source code listing of the initial segment of the model for specifying process conditions is as follows:

```

10 REM ***** MELT SPINNING OF MBM -- CIRCULAR GEOMETRY *****
20 FRHEO= 75
30 LENGTH=200          'LENGTH OF SPINLINE, IN CM.
40 DIA=.10             'IN CM.
50 W=3.25              'THROUGHPUT RATE, IN G/MIN
60 W=W/60
70 TEMP=250 : XOP=TEMP 'DIE TEMPERATURE, °C.
80 TA=21               'AVERAGE CROSS-FLOW AIR TEMPERATURE, °C
85 QAV=40              'CROSS-FLOW AIR VELOCITY, CM/SEC
90 H=.1
95 FC=0.2              ' CRYSTALLINE ORIENTATION FACTOR
100 PI=3.14159
110 GR=980
120 UCRYST=.45
130 NN=1
140 CC=225
150 CRYST=0!
160 RM=1/(.8816+.000564*TEMP)
170 U=4*W/RM/PI/DIA/DIA
180 SIGMA=4*FRHEO/PI/DIA/DIA
190 TBIR=1.2E-10*SIGMA
200 DEF FNVIS(TEMP) = .777*EXP(4585/(TEMP+273))
210 DU=SIGMA/FNVIS(TEMP)
220 RA=.0001*(12.1562-.0252737*TEMP)
230 MUA=.0002
240 FLG=1              'a counter
  
```

Solving a differential equation by the algorithm used in the present program requires that an initial condition is specified. In the case of melt spinning, the initial

condition for velocity is calculated from throughput rate, die-diameter, and die temperature using the equation of continuity (line 170). Die (or extrudate) temperature (line 70) provides an initial condition for the differential energy balance. Initial crystallinity (line 150) is always assumed zero. The initial rheological force is used as the initial condition for solving the force balance equation.

There are two aspects of melt spinning modeling. One is to check the validity of the model by comparing the predicted profiles with on-line experimental measurements. The other aspect of the modeling is to simply predict the spinline dynamics and structure development at various process conditions, once the model has been tested thoroughly. When the validity of the model needs to be tested, one measures diameter, temperature, and birefringence profiles along the spinline and rheological force near the end of the spinline at various process conditions. However, for obtaining model predictions for diameter, temperature and birefringence profile, the initial rheological force has to be known. However, the initial rheological force is extremely difficult to measure. It is possible to measure the rheological force near the end of the spinline using a tensiometer (one of the boundary conditions), but this does not give the needed initial condition. The take-up velocity provides another boundary condition. This dilemma is resolved by an iteration procedure in which a guess for the initial rheological force is made, the differential equations are solved, and the calculated boundary conditions are compared with the known boundary conditions. Changes in the initial rheological force are made until a satisfactory match is made with the boundary conditions. Thus the boundary value problem is converted into an initial value problem. However, only one of the boundary conditions can be matched precisely as it is not possible to precisely satisfy both force and velocity boundary conditions simultaneously. As the take-up velocity is more likely to be known accurately than the take-up tension, the simulation procedure involves guessing

the initial rheological force (in line 20) such that the desired take-up velocity is obtained. The predicted diameter, temperature and birefringence profiles can be compared with the experimental measurements to test the validity of the model. The predicted take-up tension should also be very close to the measured tension if the model is adequate and, the correct spinline viscosities and heat transfer coefficient correlation are used. In that case, one can be sure that rheological forces (or stresses) predicted along the spinline would be reasonably accurate. Once, the model is tested thoroughly, it can be used to predict the spinline behavior at various process conditions. In such cases, the initial rheological force (in line 20) is guessed by trial and error such that the desired take-up velocity is obtained.

The Avrami index equal to one (in line 130) is assumed in the program. The differential crystallization kinetics equation (differential Nakamura model) in the program is also written for Avrami index one. Although the program can be generalized to accept any value of Avrami index, the values of Avrami indices greater than one did not make significant difference in the prediction of on-line crystallization rates for nylon 6 (149). The stress-induced crystallization parameter (CC) was taken to be 225 in the program (line 140). The Ziabicki empirical equation (refer to Equation [2.4.18]) for describing stress-induced crystallization was used in the program. The stress-optical coefficient (equal to $1.2 \times 10^{-10} \text{ cm}^2/\text{dyne}$) was obtained using the inversion procedure (described in chapter 5) on the spinline data obtained by Bheda (17). For calculating crystalline birefringence, a value for crystalline orientation factor (FC) needs to be assumed (line 95). Crystalline orientation factor depends on the stresses in the filament during the crystallization. Bheda (17) has reported the crystalline orientation factor as a function of take-up velocity for preconditioned nylon 6 filaments maintained at a constant temperature of 70 °F and a relative humidity of 65%. At low take-up velocities the value of the

crystalline orientation factor was quite low (about 0.2), followed by rapid increase and then leveling off at quite high value (about 0.9) at high take-up velocities. For nylon 6, the ultimate crystallinity (or the maximum crystallinity that can be obtained) was assumed to be 45 percent (line 120). The spinline viscosity is specified in line number 200. Density of air was taken to be a function of temperature (line 220) and viscosity of air was assumed constant (line 230). A small step size (line 90) needs to be used for Runge-Kutta method for getting accurate results. Hence, a counter (line 240) is used in order to print and store computed spinline variables after a specified number of steps.

The melt spinning program is designed to print (on the screen or on the printer) as well as to store all important spinline variables on a floppy disk. For every run, the program prompts for the file name to store data. The program also prints all specified input process parameters on the printer so that one can know the process conditions specified. The program is designed such that any changes in the process variables must be made in the corresponding line number in the program. This is because the simulation involves guessing initial rheological force by trial and error to predict a given take-up velocity for a given set of process parameters. Hence, prompted inputs need to be absolutely minimized for each run. The section shown below opens the file on the floppy disk for storing values of spinline variables at different positions along the spinline and prints all the specified process conditions in a desired format.

```

250 INPUT "File Name =";RAJ$
260 RAJ$=RAJ$+".DAT"
270 OPEN RAJ$ FOR OUTPUT AS #1
280 PRINT "    MELT SPINNING OF MBM (CIRCULAR GEOMETRY)"
    :PRINT
290 PRINT "FRHEO =";
300 PRINT USING "###.###";FRHEO;
310 PRINT TAB(22) "MASS FLOW RATE g/min =";
320 PRINT USING "##.####";W*60;
330 PRINT TAB(55) "SPINLINE LENGTH =";

```

```

340 PRINT USING "###.#";LENGTH
350 PRINT "INITIAL TEMP. =";
360 PRINT USING "###.#";TEMP;
370 PRINT TAB(35) "H =";
380 PRINT USING "#.####";H;
390 PRINT TAB(60) "C =";
400 PRINT USING "####.#";CC
404 PRINT "QUENCH AIR TEMP. =";
405 PRINT USING "##.#";TA;
406 PRINT "          QUENCH AIR VELOCITY CM/S =";
408 PRINT USING "###.#";QAV
410 PRINT: PRINT "FILE NAME =";RAJ$
420 PRINT :PRINT
430 PRINT " DIST.  FORCE  dU/dX  STRESS  TEMP.      DIA.(MI)
V(M/MIN) %CRY"
440 PRINT
450 PRINT USING "###.##  ###.#  ###.##  ##.##^  ###.#  ###.##
####.###.###";X,FRHEO,DU,SIGMA,TEMP,DIA*10000, U*.6, CRYST*100

```

The line 430 gives the heading of various variables that can be printed either on screen (if PRINT statement is used) or on printer (if LPRINT statement is used). The line 450 prints the listed spinline variables in a desired format in a tabular form. The program solves the above specified simultaneous differential equations at each step size increment and prints (and stores on floppy) the spinline variables in a tabular form after a fixed step size specified using the counter. The above specified step size is reduced ($H=0.005$) if stress-induced crystallization is triggered on the spinline.

Using the process conditions specified in the program statements (line numbers 30 to 200), the procedure to predict the spinline diameter, temperature, stress, birefringence and crystallinity profiles for the take-up speed of 2000 m/min is as follows. As described earlier, the initial rheological force needs to be specified by trial and error to obtain the desired take-up velocity. The tabulation of various initial rheological forces tried and corresponding predicted take-up velocities are given in Table 2.

The Spinneret shape used in industrial melt spinning processes can be different from a circular shape. For example, for producing carpet fibers, the spinneret used often has a "Y" shape from which trilobal filaments are obtained. The shape of the spinneret

Table 2. Tabulation of initial rheological forces tried and corresponding predicted take-up velocities.

F_0 (dynes)	V_L (m/min)
50	F_{rheo} and $dV/dz < 0$ for $z > 12$ cm.
60	F_{rheo} and $dV/dz < 0$ for $z > 22$ cm.
70	F_{rheo} and $dV/dz < 0$ for $z > 194$ cm.
75	7520 m/min
72.5	530 m/min
73.5	1085 m/min
74	1780 m/min
74.2	2290 m/min
74.1	2005 m/min

and running spinline has significant influence on the spinline kinematics and dynamics. Increased specific surface area in the case of trilobal fibers makes heat transfer more intensive and consequently leads to more rapid solidification. This leads to a shortening of the deformation zone in the spinline (the filament drawdown would occur nearer the spinneret), an increase in average velocity gradients, and increase in stresses and the degree of average amorphous orientation. The "Y" shaped spinneret, from which trilobal filaments are obtained, can be approximated using an equilateral triangular shape spinneret with the appropriate cross sectional area and with the assumption of no shape change along the spinline. For the triangular spinneret, the basic governing equations and various properties relationships for the mathematical model are the same as those for a circular cross section spinneret. There were two basic changes applied to the model for triangular spinneret. The first one is to express the heat transfer and the air drag for triangular shape and the second to express deformation in terms of equivalent diameter calculated from cross sectional area, to compare results with those for a circular spinneret. The effective diameter for triangular spinneret shape (of side S) can be obtained as follows:

$$\frac{\pi D_{\text{eff}}^2}{4} = \frac{\sqrt{3}}{4} S^2 \quad [4.1.1]$$

$$D_{\text{eff}} = \sqrt{\frac{\sqrt{3}}{\pi}} S \quad [4.1.2]$$

Also, the heat transfer coefficient calculated using the inversion procedure does not take into account the effect of a cross-air flow which is used in the industrial melt

spinning processes. Kase and Matsuo (7) have studied the effect of cross-air flow on the heat transfer coefficient and have obtained a correction term to take into account the effect of cross-air flow. The heat transfer coefficient without the cross flow was obtained using the Inversion procedure on the data for MBM resins. Using their correction term, the heat transfer coefficient used to model spinning processes with cross-air flow is as follows:

$$HTC = 1.47 \times 10^{-4} \left[\frac{Vel}{Area} \right]^{0.266} \left[1 + 8 \left(\frac{u_c}{Vel} \right)^2 \right]^{1/6} \quad [4.1.3]$$

The apparent elongational viscosity data correlated with Arrhenius temperature dependence for various nylon 6 resins can not be used to compute spinline elongational viscosity near the glass transition temperature T_g . A much better equation near T_g is the Williams-Landel-Ferry (or WLF) equation (refer to equation [2.2.5]). A WLF equation with $c_1=8.86$ and $c_2=101.6$ °K along with a suitable reference temperature T_0 is shown to provide a better fit near T_g with the available literature data. For many polymers, the reference temperature chosen in this manner is found to be $T_g + 50$ within ± 5 °K. Using $T_g = 40$ °C for nylon 6, for temperature below 100 °C, a WLF type equation was used to model spinline viscosities as shown below:

$$\eta = C_0 \exp \left[\frac{-8.86(T - 90)}{101.6 + T - 90} \right] \quad [4.1.4]$$

where C_0 is obtained by matching the Arrhenius type apparent elongational viscosity expression at 100 °C.

Assumption of Newtonian rheological behavior in the spinline model may not be

adequate in the case of melt spinning of polyolefins. In such cases, one may have to consider a non-Newtonian inelastic (viscous-thinning) or non-Newtonian viscoelastic constitutive equation to describe spinline rheological behavior. A formulation of non-Newtonian inelastic and non-Newtonian viscoelastic analysis of melt spinning is given in Appendix.

CHAPTER 5

ANALYSIS OF CN 9984 AND BHS SPINLINE DATA

The basic purpose of the present research is to develop an improved process model for melt-spinning of fibers with a better understanding of polymer rheology and polymer physics underlying the spinline behavior. The improved Newtonian spinline model described earlier in chapter 4 can be tested by comparing its predictions with the experimental data. Because of the existence of the experimental data on CN 9984 and BHS nylon 6 resins obtained by Bheda (17,18), the results of the mathematical simulation based on the improved model are compared directly to the experimentally measured diameter, temperature and birefringence profiles. These comparisons would assess the ability of the model to simulate the experimentally observed behavior.

However, the quality of predictions made by any mathematical model is highly dependent on the quality of input data. Quantities required for spinline simulation include resin density and heat capacity as a function of temperature, stress-optical coefficient, intrinsic amorphous and crystalline birefringence, apparent spinline elongational viscosity and heat transfer coefficient. The latter two quantities are rarely known with precision, if at all. Consequently, Bheda used some of the on-line experimental measurements to obtain spinline elongational viscosity as a function of temperature and heat transfer coefficient following the procedure of Deeg and George(19). This approach (called the "inversion procedure") has since been modified and improved upon by the author to yield better results. The improved inversion procedure has also been implemented on an IBM-PC. The results obtained using this improved inversion procedure are presented here and are examined in the context of the pseudoplastic nature of polymer melts.

5.1 Inversion Procedure and Evaluation of Elongational Viscosity and Heat Transfer Coefficient

An "inversion procedure" for evaluating the apparent elongational viscosity of polymer melt from spinline data was described earlier in Chapter 2. The spinline viscosity data can be obtained from on-line measurements of diameter and temperature along the molten portion of a spinline and a single tension measurement towards the end of the spinline (17,18). The experimental diameter and temperature profiles and the tension measured at the bottom of the spinline are used to compute the rheological force and hence, the spinline stress profile along the spinline using integration of the differential force balance equation [2.1.4]. The ratio of stress to elongation rate at each point on the spinline then gives the apparent elongational viscosity along the spinline, which can be correlated with the spinline temperature profile. The inversion procedure involved smoothing the diameter and temperature profiles using suitable fitting functions to compute elongation rate and temperature gradient, respectively. In the analysis of Bheda (17,18), the diameter profiles were directly fitted using a very high order polynomial (of 8-10th order). This high order polynomial was necessary to accommodate the flattened diameter profile in the bottom half of the spinline. However, this procedure led to spurious "bumps" in the calculated elongation rate profile in the bottom half and hence, a scatter in the apparent elongational viscosity data (17,18). Thus, a better smoothing procedure is necessary to reduce the scatter and to yield better results.

Such flattened diameter profiles are also obtained in isothermal gravity spinning experiments as reported by Patel and Bogue (32,33). They successfully used a polynomial fit of reciprocal diameter ($1/D$) versus spinline distance to obtain the apparent elongational viscosity data. In fact, the generalized sine function fitting of the diameter

data based on the isothermal Newtonian low-speed spinning theory developed by Patel and Bogue (33) gave identical results as those based on empirical polynomial fitting of $(1/D)$ versus spinline distance. Hence, based on these literature results, a modified inversion procedure involving a polynomial fit of $(1/D)$ versus spinline distance (of 4-6 order) can be used to calculate the elongation rates and the apparent elongational viscosity. The choice of the order of the polynomial would depend upon the data set. The order should be high enough to pick up the trends in the data set, giving an average result without following the scatter in detail. There is a statistical procedure whereby one may test successively increasing orders of polynomials until one reaches a non-significant result (152). In the case of fitting $(1/D)$ versus axial distance data, a minimum of a second degree polynomial would have to be used to give a maximum in the elongation rate profile (which would be the case at lower throughput rate and at lower take-up velocities). Note that as the velocity is proportional to $(1/D)^2$, this procedure is a way of fitting the velocity profile with the equivalent of a higher degree polynomial. Once a fitted polynomial is obtained using any suitable statistical package, it can be used to compute elongation rates along the spinline. The elongation rates (dV/dz) are obtained from differentiating the polynomial curve fitting equation (e.g. of fourth order) for $1/D$ as follows:

$$\begin{aligned}
 1/D &= a + bz + cz^2 + dz^3 + ez^4 \\
 dD/dz &= -D^2 (b + 2cz + 3dz^2 + 4ez^3) \\
 dV/dz &= (-8w/\pi D^3) dD/dz
 \end{aligned}
 \tag{5.1.1}$$

A schematic diagram of the inversion procedure for computing the apparent spinline elongational viscosity and heat transfer coefficient is shown as Figure 5.1. A computer program for carrying out the computations of elongation rate, stress, the

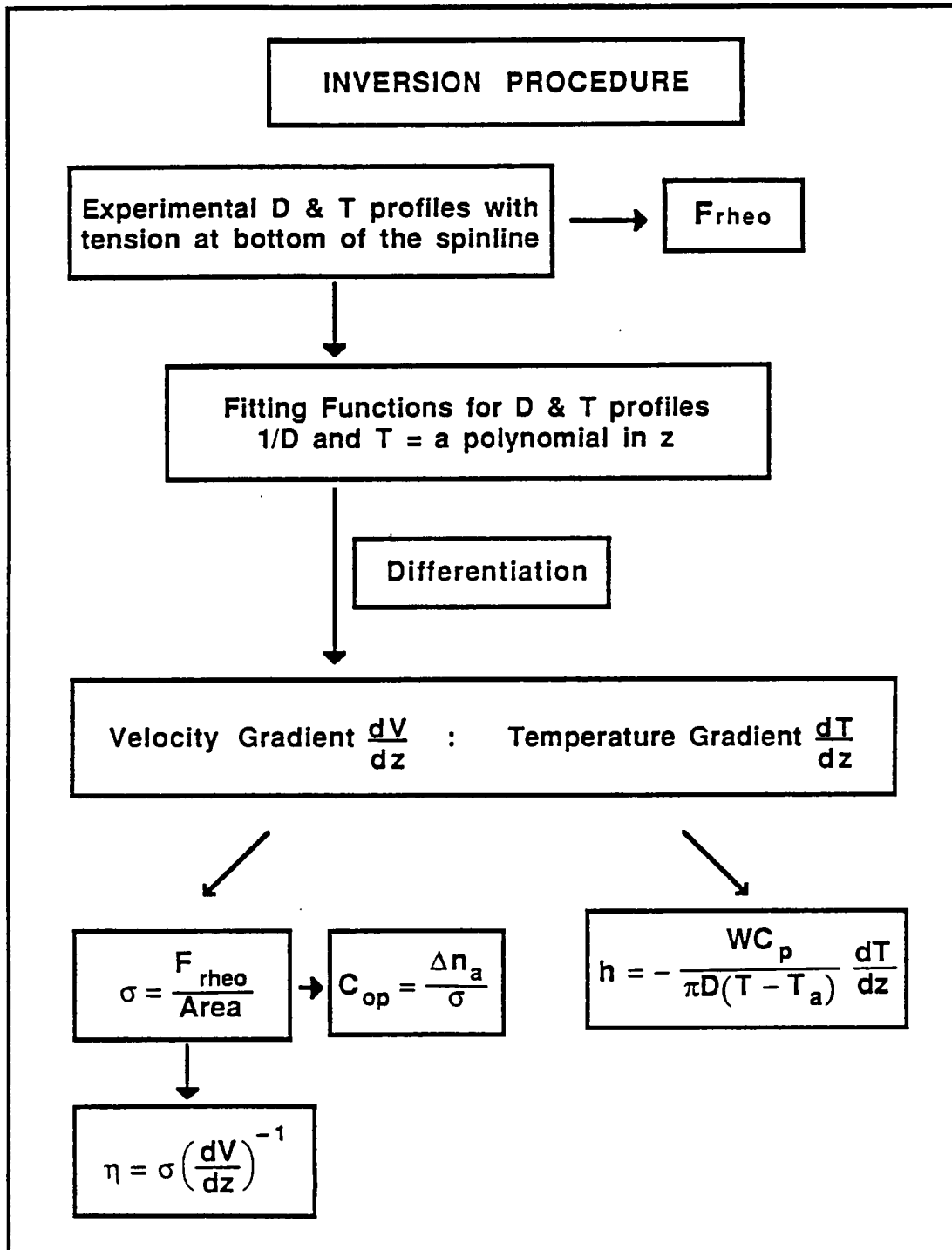


Figure 5.1. Schematic diagram of the inversion procedure for computing the apparent elongational viscosity and heat transfer coefficient from experimental on-line measurements of spinline diameter, temperature and tension.

apparent elongational viscosity, and the heat transfer coefficient along the spinline was written in BASIC and implemented on an IBM PC using TURBOBASIC compiler. The same experimental data used by Bheda (17,18) were reanalyzed using this modified inversion procedure. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for BHS resulting from this reanalysis is shown in Figure 5.2. The results are compared with the three-times the zero-shear viscosity (so-called "Trouton viscosity") data of BHS.

First of all, It can be observed from Figure 5.2 that the resulting viscosity data are considerably smoother than the previous calculations (17,18). This mainly is due to better smoothing of diameter data using a polynomial fit of reciprocal diameter profile and the resulting accurate calculation of the elongation rate profile. Small diameters and smaller diameter changes in the bottom half of the spinline are magnified by taking the inverse. The improvement probably results from a favorable change in the error distribution and statistical weights of the data points compared to the previous procedure. The viscosity data near the die may not be accurate due to die-flow effects and also because error in the measured take-up force would give a larger error in the calculation of rheological force near the die.

It can also be seen that the computed spinline elongational viscosity values are lower than Trouton viscosity data and also the apparent activation energy (slope of the curves) is also less than the zero-shear activation energy. This is likely due to the deformation thinning (pseudoplastic) nature of polymer melts. Zhou (20) in his study of nonisothermal spinning of a 300 MFR polypropylene resin, reports an activation energy which is about four times less than that obtained from zero-shear viscosity measurements done by Patel (32).

Also the spinline viscosity data are somewhat different for different mass

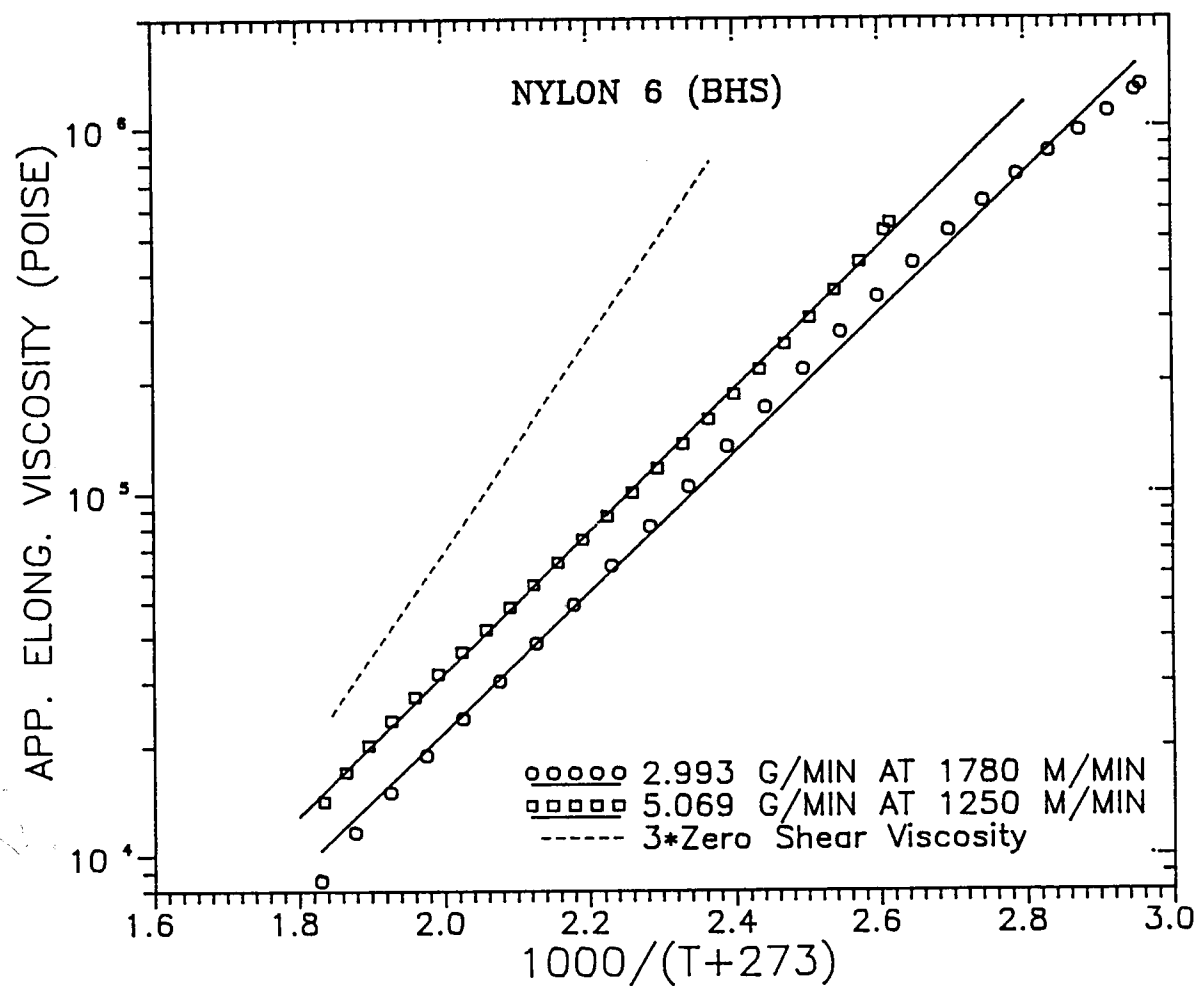


Figure 5.2. Calculated apparent elongational viscosity using improved inversion procedure and zero-shear viscosity for BHS resin at two throughput rates.

throughput rates even though each viscosity function follows nearly the Arrhenius temperature dependence. In all the cases examined, a higher apparent elongational viscosity at a given temperature corresponded to a lower instantaneous elongation rate or stress. The reason for the difference may be attributed to the fact that most polymers, including nylon 6, exhibit non-Newtonian (deformation-thinning) viscoelastic behavior and their viscosities depend on their instantaneous deformation rate and deformation histories apart from temperature. Such differences may also be a result of error in tension measurements. It is interesting to note that such differences (though not large) are obtained for nylon 6 even though nylons exhibit Newtonian behavior in shear over a broad shear rate range. The scatter in the calculated viscosity data of Bheda (17,18) masked the systematic differences that we have now observed using the improved procedure. Similar results were obtained for CN 9984 resin. Cernia and Conti (143) have reported similar results. Hill and Cuculo (144), in an empirical approach, seek to describe their PET data by a linear dependence of the logarithm of the apparent elongational viscosity on the reciprocal of temperature, the strain rate, and the product of these two variables. This gave an activation energy which is a decreasing function of strain rate.

As noted earlier, the gradient of temperature profile can be used to evaluate the heat transfer coefficient along the spinline. For smoothing the temperature data, a second degree polynomial fitting of temperature versus distance data was used. The results for both the resins for two throughput rates are plotted as Figure 5.3. It can be observed that the data for four different cases fall on a straight line as would be desired. The calculated correlation for the heat transfer coefficient is

$$\text{HTC} = 9.287 \times 10^{-5} \left[\frac{\text{Vel}}{\text{Area}} \right]^{0.287} \quad [5.1.2]$$

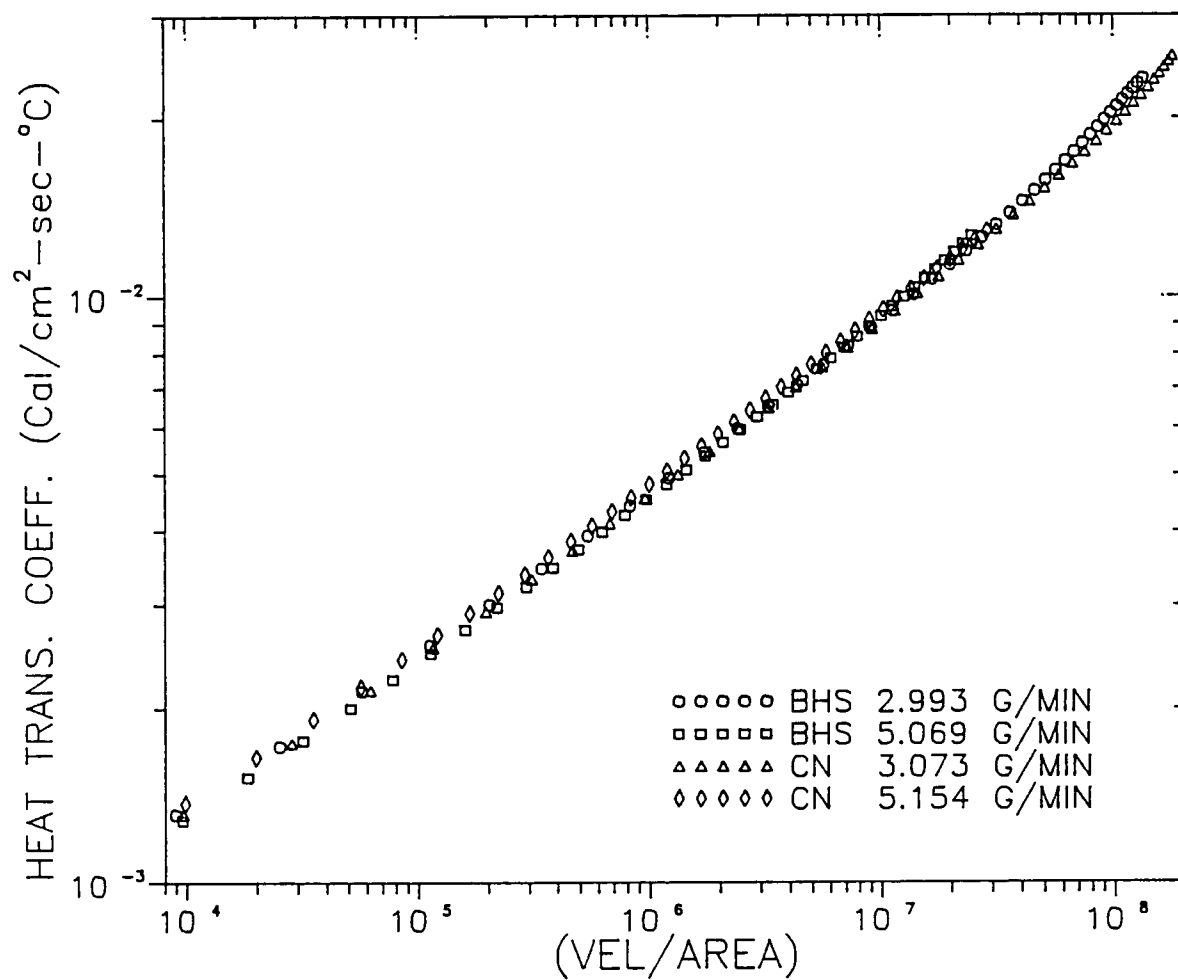


Figure 5.3. Calculated heat transfer coefficient correlation using improved inversion procedure for BHS and CN 9984 resins each for two throughput rates.

where cgs units have been used for fiber velocity and cross-sectional area.

Such an "inversion procedure" is very helpful as it gives values of the extensional viscosity for a given resin and heat transfer coefficient data for a given experimental set-up. Also, using the computed stress profile and measured birefringence profile, the stress-optical coefficient can be calculated.

The differences in computed apparent elongational viscosity data are disregarded in the present model calculations and the Newtonian viscosity model is assumed. The required Arrhenius temperature dependent equations were obtained from averaging the data of Figure 5.2. The resulting expressions for apparent elongational viscosity in poise are for CN9984

$$\eta = 0.404 \exp\left[\frac{5140}{T + 273}\right] \quad [5.1.3]$$

and for BHS

$$\eta = 3.517 \exp\left[\frac{4470}{T + 273}\right] \quad [5.1.4]$$

These results will be used as input parameters to the spinline model, instead of literature values. The effect of crystallinity on viscosity is very difficult to quantify. It was assumed to be of the form (15)

$$\eta(T, X_c) = \eta(T) \exp\left[4\left(\frac{X_c}{X_\infty}\right)^2\right] \quad [5.1.5]$$

5.2 Mathematical Modeling

The mathematical model used in this study is described in detail in chapter 4. As

discussed earlier, in the present calculations of the model we assume that the rheological behavior of the polymer may be described in terms of a Newtonian constitutive equation. The crystallization kinetics are described in terms of a differential Nakamura model equation [2.4.14] with a temperature and molecular orientation dependent rate parameter K from equation [2.4.8] and [2.4.18] (Ziabicki's empirical formulation). It is assumed that the molecular orientation in the amorphous polymer melt can be computed from the rheo-optical law. The resulting equations that must be solved simultaneously to mathematically simulate the melt spinning process are summarized in Figure 4.1. The simulation was carried out using key relationships obtained from the inversion procedure and the literature values of other physical parameters. The solution procedure is based on an iterating scheme in which initial rheological force is varied until the take-up velocity condition is satisfied.

As noted above, it is necessary to have a considerable amount of input of physical property data for the model. The density (gm/cc) of nylon 6 was considered to be temperature and crystallinity dependent (145):

$$\rho = \frac{1}{\left[(0.8816 + 5.64 \times 10^{-4} \cdot T) - (0.0292 + 3.26 \times 10^{-4}) \cdot X_c \right]} \quad T < T_m \quad [5.2.1]$$

The heat capacity (cal/gm/°K) was taken to be (146)

$$C_p = 3.229 \times 10^{-4} (T+273) + 0.4739 \quad [5.2.2]$$

The correlation for air drag coefficient, C_d , was taken to be $C_d = 0.27 \text{ Re}^{-0.61}$ (15). For nylon 6 the stress optical coefficient, C_{op} , was computed from online measurements using the inversion procedure. The value obtained was $C_{op} = 1.2 \times 10^{-10}$

cm²/dyne. Shimizu et al. (15) have reported $C_{op} = 0.9-1.8 \times 10^{-10}$ cm²/dyne from online measurements. The intrinsic amorphous birefringence, Δ_a , and intrinsic crystalline birefringence, Δ_c , were considered to be constant at values of $\Delta_a=0.0825$ and $\Delta_c=0.0963$ (147). The heat of fusion was taken as 45 cal/gm (21). The crystalline orientation factor was assumed to be $f_c=0.9$. The ultimate crystallinity (X_∞) was assumed to be 45 percent.

The results of the modeling for BHS resin for two throughput rates are compared with the experimental diameter, temperature and birefringence profiles in Figures 5.4-5.9. In these figures the plotted points are the experimental measurements, while the curves represent the calculations from the model. As can be seen from these figures, the model predictions match the experimental data quite well. Similar comparisons for CN9984 resin at lower throughput rate are shown as Figures 5.10-5.12. Again, the model predictions match the experimental data quite well. The computed crystallinity profiles for CN9984 resin are shown in Figure 5.13. The computed temperature profiles to illustrate the effects of mass throughput rate and the resin molecular weight are shown in Figure 5.14.

The predicted and the experimentally measured take-up forces are compared in Table 3 and 4 for BHS and CN 9984 resins, respectively. The predicted values match the experimental take-up forces reasonably well. It can be seen from Figures 5.8 and 5.12 that, for each resin at lower throughput rate, predicted birefringence values are higher than the experimental data. This may be because of using averaged viscosity in the model calculation. This led to using higher viscosities for lower throughput rates, resulting in higher spinline stresses and higher amorphous birefringence. The higher birefringence values predicted for the cases of on-line crystallization may also partially be due to higher assumed values of crystalline birefringence contribution. The similar discrepancies

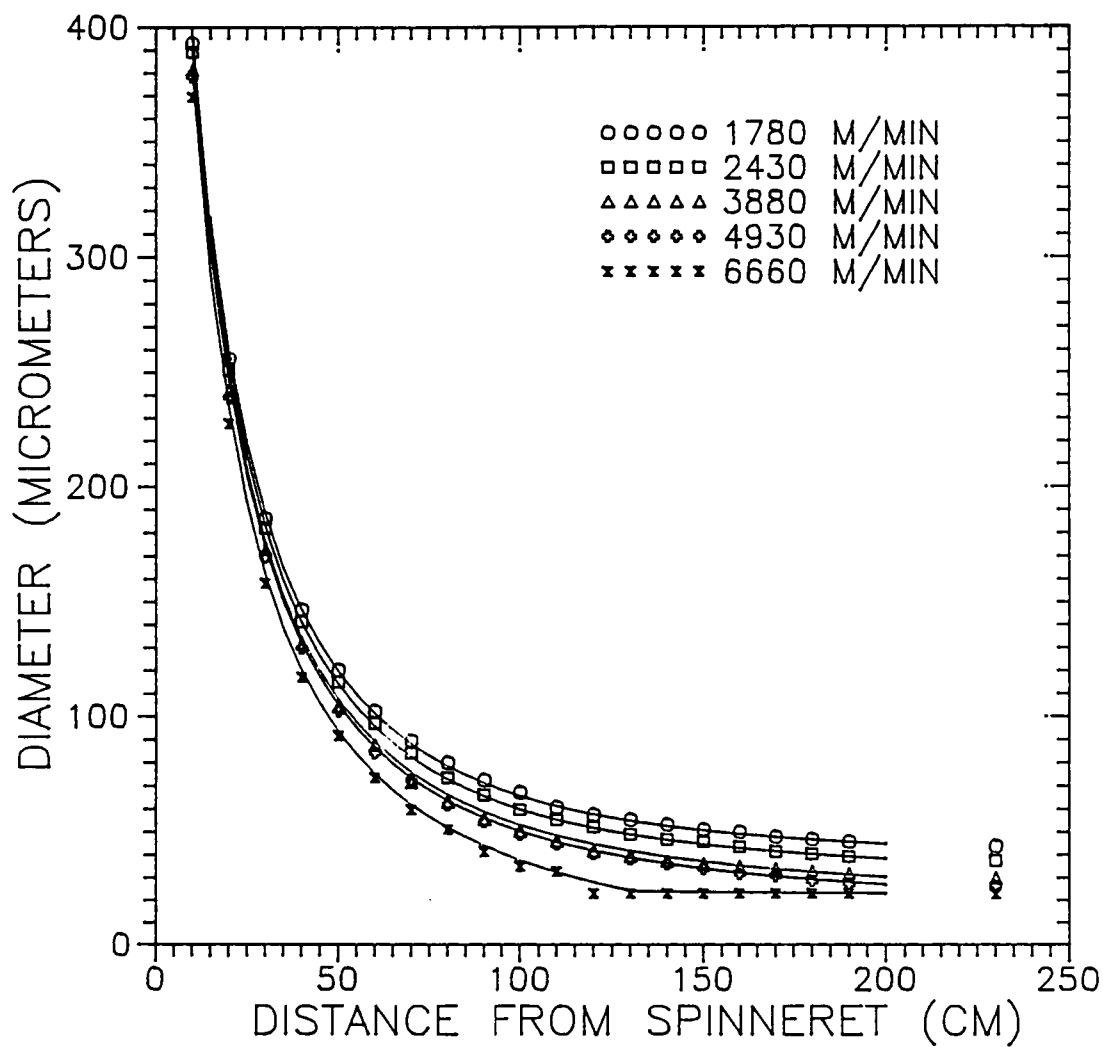


Figure 5.4. Comparison of the model predictions with the on-line diameter measurements for BHS resin melt spun with a mass throughput of 2.993 g/min.

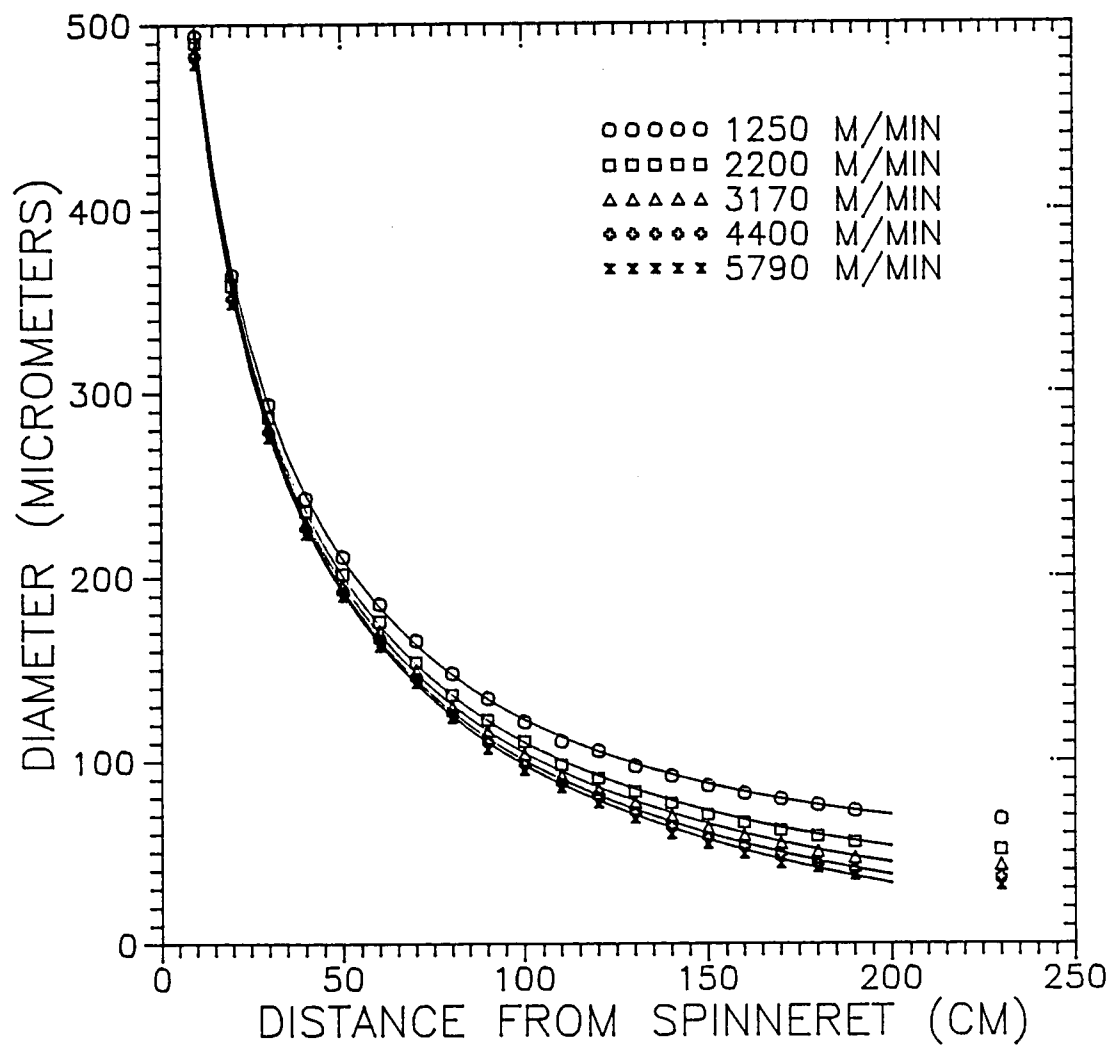


Figure 5.5. Comparison of the model predictions with the on-line diameter measurements for BHS resin melt spun with a mass throughput of 5.069 g/min.

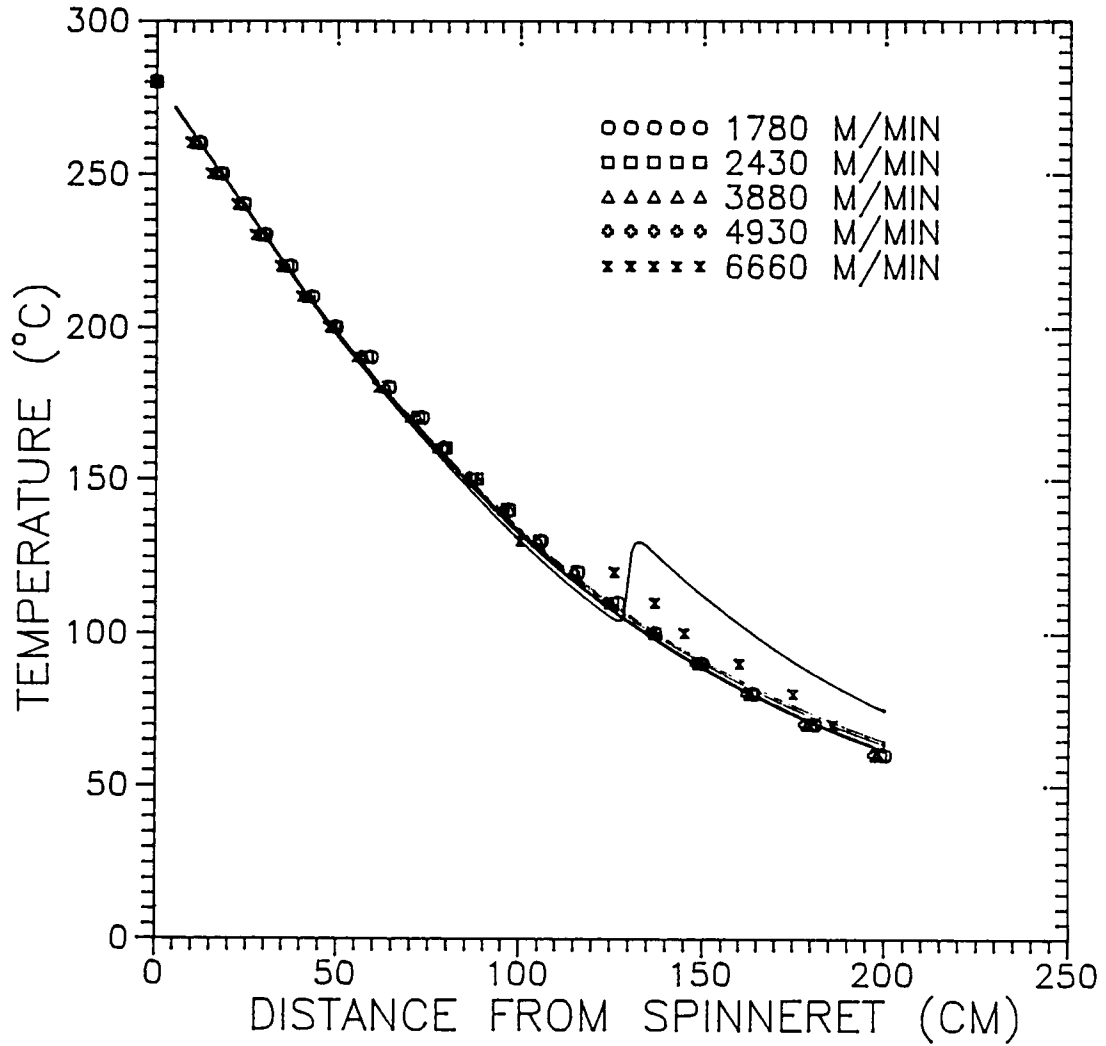


Figure 5.6. Comparison of the model predictions with the on-line temperature measurements for BHS resin melt spun with a mass throughput of 2.993 g/min.

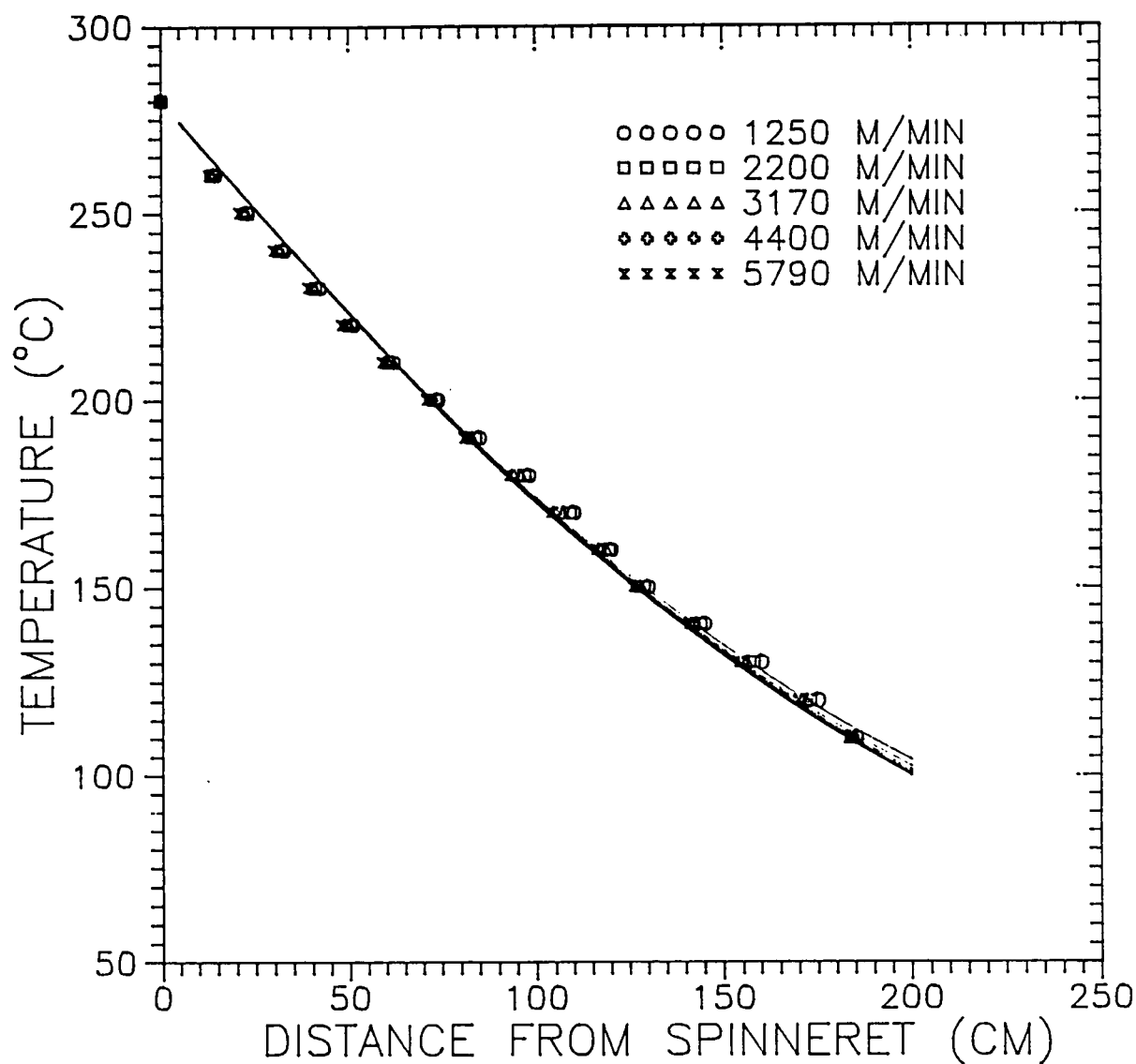


Figure 5.7. Comparison of the model predictions with the on-line temperature measurements for BHS resin melt spun with a mass throughput of 5.069 g/min.

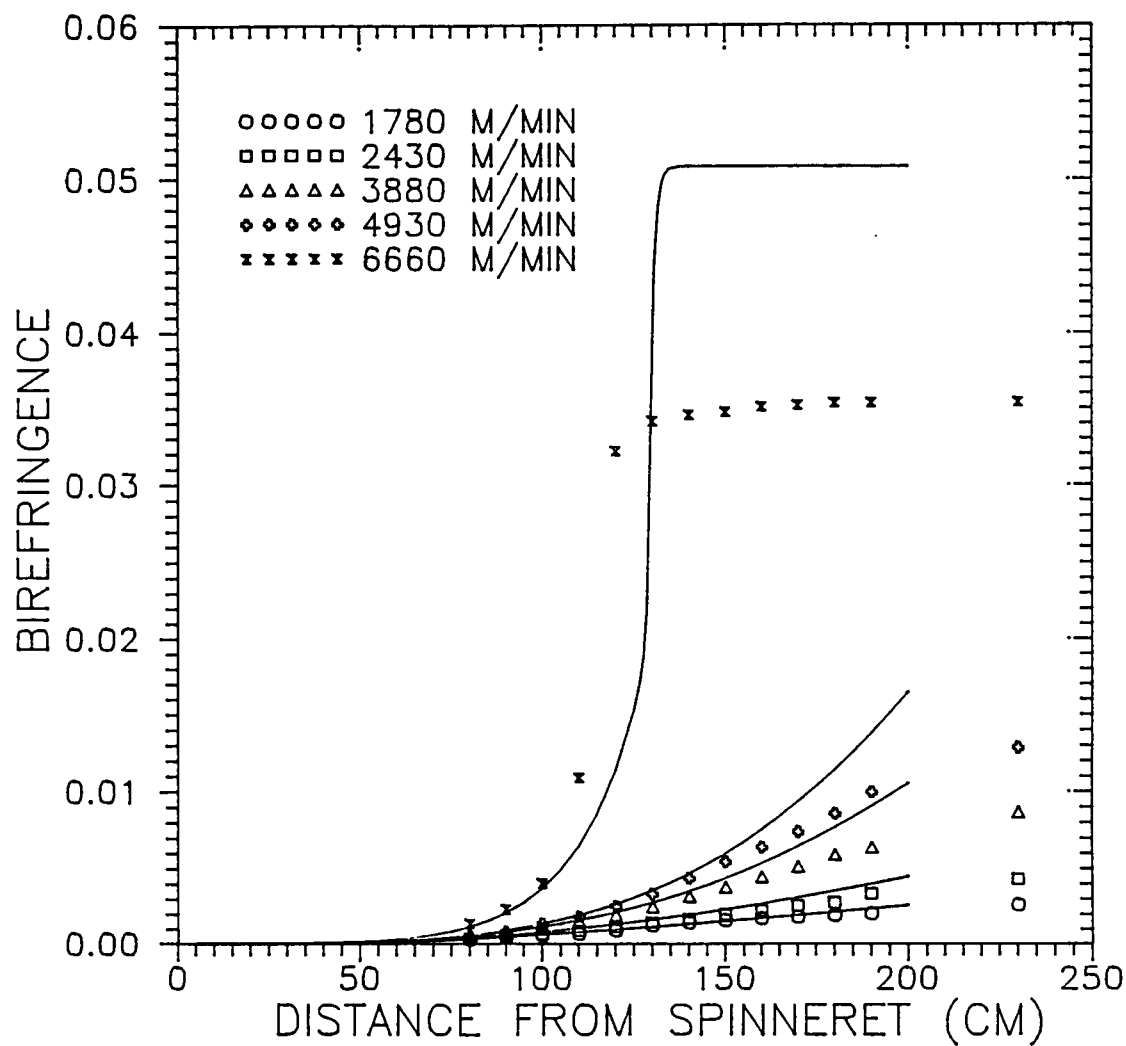


Figure 5.8. Comparison of the model predictions with the on-line birefringence measurements for BHS resin melt spun with a mass throughput of 2.993 g/min.

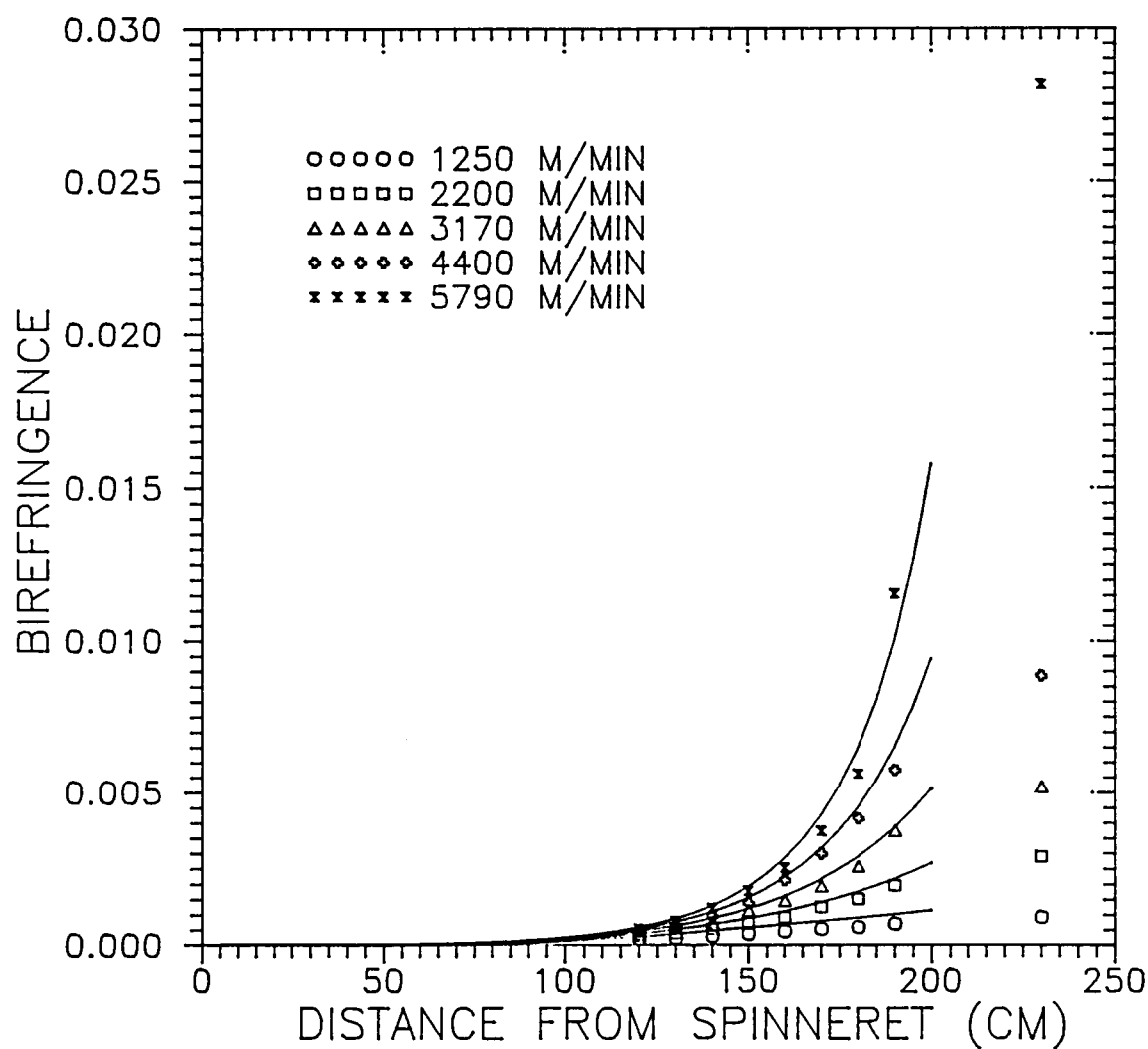


Figure 5.9. Comparison of the model predictions with the on-line birefringence measurements for BHS resin melt spun with a mass throughput of 5.069 g/min.

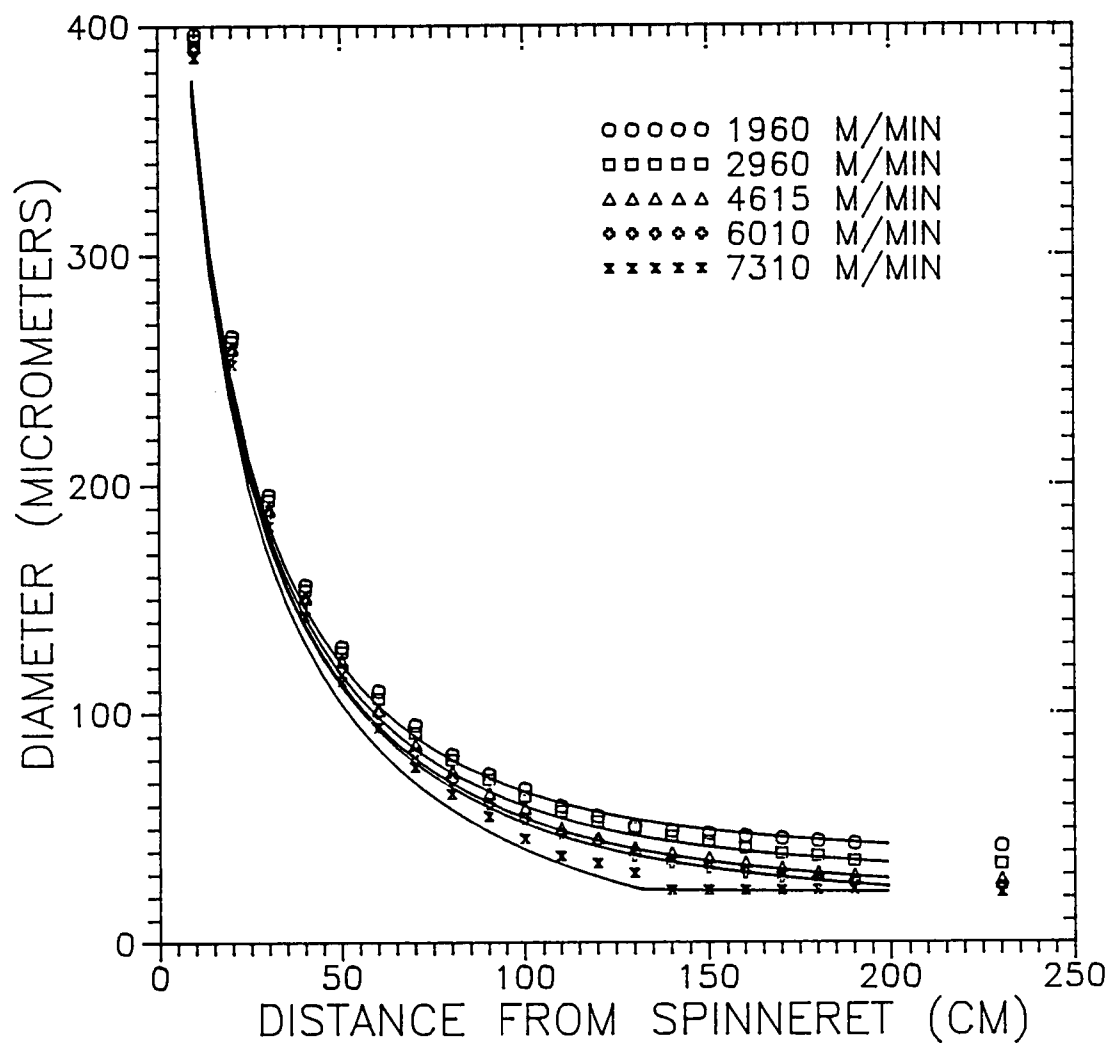


Figure 5.10. Comparison of the model predictions with the on-line diameter measurements for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.

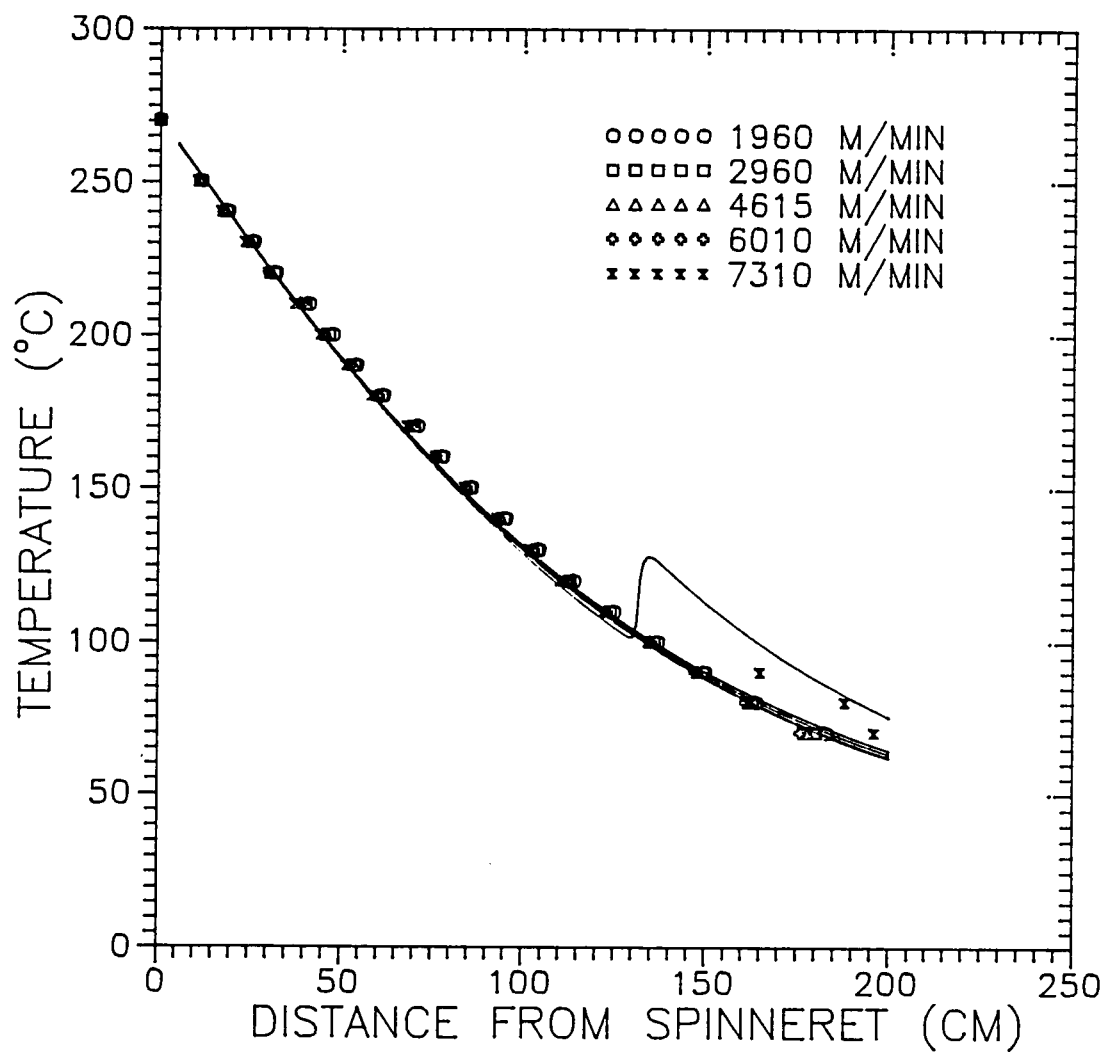


Figure 5.11. Comparison of the model predictions with the on-line temperature measurements for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.

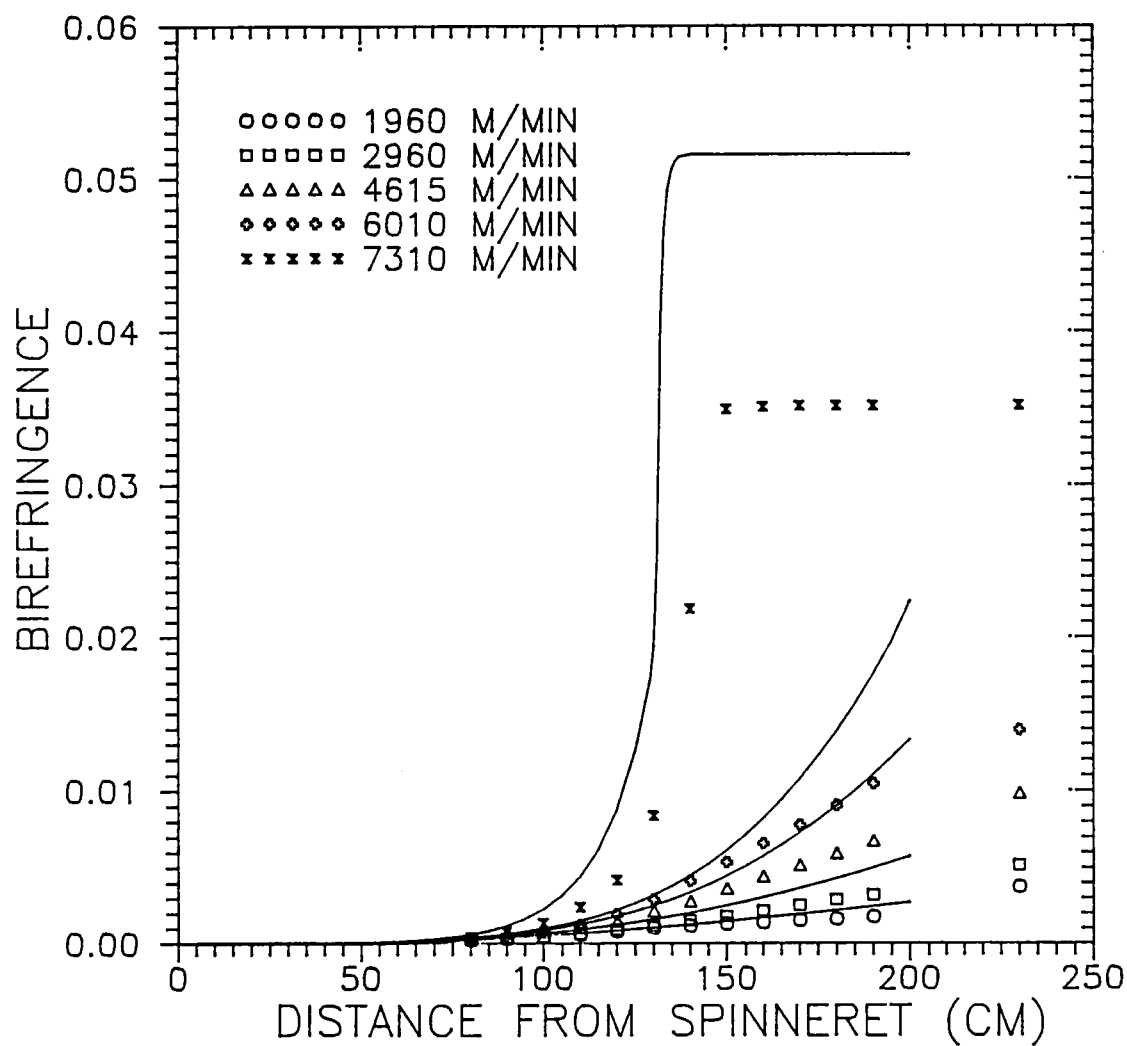


Figure 5.12. Comparison of the model predictions with the on-line birefringence measurements for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.

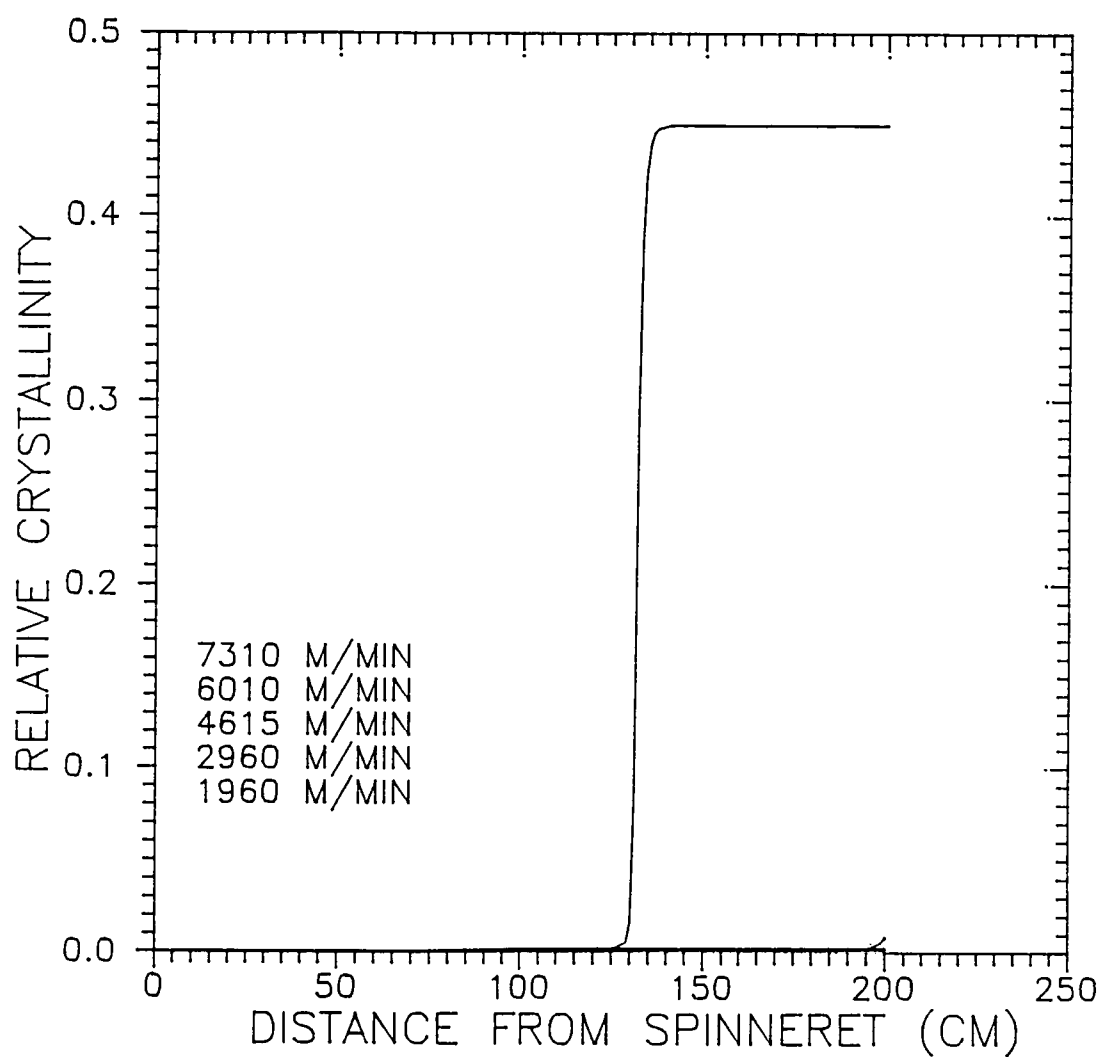


Figure 5.13. Computed crystallinity profiles for CN 9984 resin melt spun with a mass throughput of 3.069 g/min.

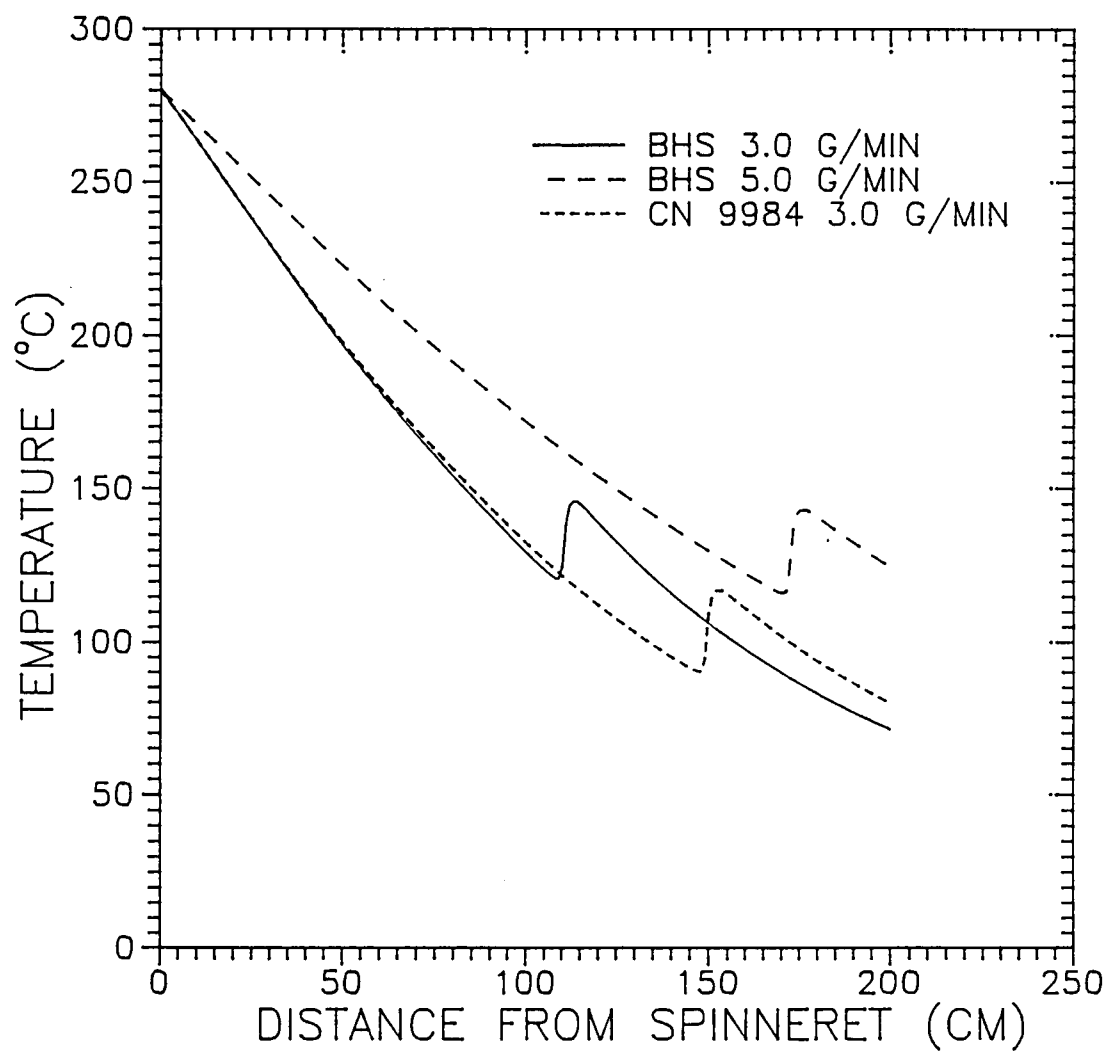


Figure 5.14. Effects of mass throughput rate and the resin molecular weight on the simulated temperature profiles at a take-up velocity of 7000 m/min.

Table 3. Comparison of predicted take-up force with the experimentally measured values for CN 9984 resin

CN 9984 3.069 g/min			CN 9984 5.154 g/min		
Take-up velocity m/min	Experimental dynes	Predicted dynes	Take-up velocity m/min	Experimental dynes	Predicted dynes
1960	274.4	281.4	1570	284.2	256.4
2960	333.2	406.4	2560	421.4	394.1
4615	450.8	599.5	3885	588.0	554.3
6010	539	750.4	5180	720.3	692.6
7310	960.4	1168.5	6455	823.2	812.2

Table 4. Comparison of predicted take-up force with the experimentally measured values for BHS resin

BHS 2.993 g/min			BHS 5.069 g/min		
Take-up velocity m/min	Experimental dynes	Predicted dynes	Take-up velocity m/min	Experimental dynes	Predicted dynes
1780	279.3	295.6	1250	269.5	248.3
2430	347.9	382.0	2200	426.3	397.9
3880	475.3	562.8	3170	563.5	534.2
4930	553.7	685.8	4400	725.2	691.2
6660	999.6	1126.8	5790	842.8	851.3

observed in Table 3 and 4 may also be because of taking averaged elongational viscosity in the model calculations, resulting in higher predicted take-up tension for the lower throughput cases. A higher value of air drag coefficient, especially near the aspirator, may also be a contributing factor. It can be seen that the model did not predict "necking" or sudden diameter drawdown observed for both the resins at the lower mass throughput rate at the highest spinning speeds.

The stress-induced crystallization parameter, $C=225$ was used in these simulations. The parameter C characterizes the enhancement of crystallization rate due to orientation. The value of the parameter C as incorporated in the model for nylon 6 predicts whether or not crystallization will occur on-line and if it occurs, where on the spinline it is triggered. Because of the above mentioned limitations of the empirical equations describing stress-induced crystallization, crystallization rates are overpredicted in the later stages of crystallization. This was manifested in the prediction of much higher temperature rise by the model than the temperature rise experimentally observed at high spinning speeds. Similar observations were also made for polypropylenes at higher spinning speeds (148). Therefore, in the above calculations, the crystallization rate was not allowed to exceed $10,000 \text{ sec}^{-1}$. This is equivalent to assuming that the crystallization rate saturates at this value. The Avrami index $n=1$ was used in the calculations. Different values of index n did not significantly affect the calculations as previously noted by Ziemiński and Spruiell (13,14).

The simulated and the experimental results give considerable insight into the role of various process and resin variables in controlling the structure and properties of melt spun filaments. Figures 5.10 through 5.13 show the computed and the experimental velocity, temperature, birefringence and crystallinity profiles for the lower molecular weight resin for filaments spun over a range of spinning speeds from 1960 m/min to

7310 m/min. At the lowest spinning speed the filament does not crystallize during spinning due to the slow crystallization kinetics of nylon 6. This is in spite of the fact that the lowest spinning speed corresponds to the slowest cooling rate through the range of temperatures where molecular mobility is sufficient for crystallization to occur. The molecular orientation, as measured by the birefringence, is also low in this sample throughout the spinpath. As the take-up velocity increases, the molecular orientation in the melt increases; this produces a very large increase in the crystallization rates and triggers crystallization in the spinline at spinning speeds above about 6000 m/min. The occurrence of crystallization during spinning is accompanied by a recalescence or plateauing in the temperature profile due to the heat of crystallization being converted to sensible heat as shown in Figure 5.11. Under these conditions crystallization produces a rapid rise in the birefringence along the spinline due to oriented nucleation and growth of crystals, and it causes a flattening of the velocity or diameter profiles due to the rapid increase of viscosity caused by the crystals.

The effects of polymer mass flow rate on the spinline dynamics can be observed in Figures 5.4-5.9 and is illustrated in Figure 5.14. Increasing the mass flow rate of the polymer through the spinneret hole at a given take-up velocity substantially reduces the polymer cooling rate and spinline stress; this lowers the rate of development of molecular orientation along the spinline and moves the point at which crystallization begins further from the spinneret. As shown in Figure 5.14, BHS resin spun with a mass throughput rate of 5.0 g/min and at 7000 m/min crystallizes on the spinline. However, for the same final denier filament spun at a throughput rate of 3.0 g/min, take-up velocity has to be 4180 m/min and in that case the filament does not crystallize on the spinline.

The effects of polymer molecular weight on spinline dynamics can be observed in the above figures and is also illustrated in Figure 5.14. Increasing the polymer molecular

weight for a given set of spinning conditions results in increased spinline stresses; this enhances the development of molecular orientation along the spinline and moves the point at which crystallization begins towards the spinneret. The effect of molecular weight on the simulated profiles is introduced through the increase in viscosity caused by the increased molecular weight.

The mathematical simulation and the experimental results make it quite clear that crystallization in the spinline is controlled by a competition between crystallization kinetics, which are largely controlled by the level of molecular orientation, and the cooling rate, which is controlled by the mass flow rate, spinning speed and cooling medium. The balance of this competition determines whether crystallization will occur and the temperature at which it occurs. Whenever the effect of increased molecular orientation overwhelms the effect of increased cooling rate an increase of spinning speed will result in an increase in the temperature at which crystallization occurs. But when the effect of cooling rate is more significant than the influence of molecular orientation, the temperature of crystallization will decrease with an increase of spinning speed. If the crystallization rate becomes too low, then the polymer does not crystallize during spinning and the filament vitrifies into a glass on cooling below the glass transition temperature.

CHAPTER 6

CRYSTALLIZATION KINETICS DURING PROCESSING -- ANALYSIS OF AVAILABLE APPROACHES

The mathematical modeling of spinline crystallization requires a nonisothermal description of crystallization and a knowledge of crystallization rate as a function of temperature and molecular orientation. In this chapter, an analysis of available methods of dealing with polymer crystallization for process modeling is presented. Problems encountered in using isothermal data to predict nonisothermal crystallization are discussed and illustrated using experimental data on BHS and MBM-I resins. A nonlinear regression method is presented for directly fitting nonisothermal crystallinity data using the Nakamura model to obtain crystallization rate equation parameters. Two empirical methods for including amorphous orientation effects are also considered and evaluated by comparing predicted results to online experimental data for melt spinning of BHS resin.

6.1 Quiescent Isothermal Kinetics

As mentioned in chapter 2, crystallization rates are usually measured under quiescent, isothermal conditions, and, in the case of nylon 6, they are experimentally accessible only over a narrow temperature range at low undercoolings. The isothermal kinetics data obtained at various temperatures for BHS and MBM-I resins are shown in Figures 6.1 and 6.2, respectively. The Avrami analysis of these data for relative crystallinity between 10 and 90 percent are shown in Figures 6.3 and 6.4, respectively. It can be seen from Figures 6.1 and 6.2 that the time taken for half of the crystallization to develop ($t_{1/2}$, a measure of crystallization rate) is a strong function of crystallization

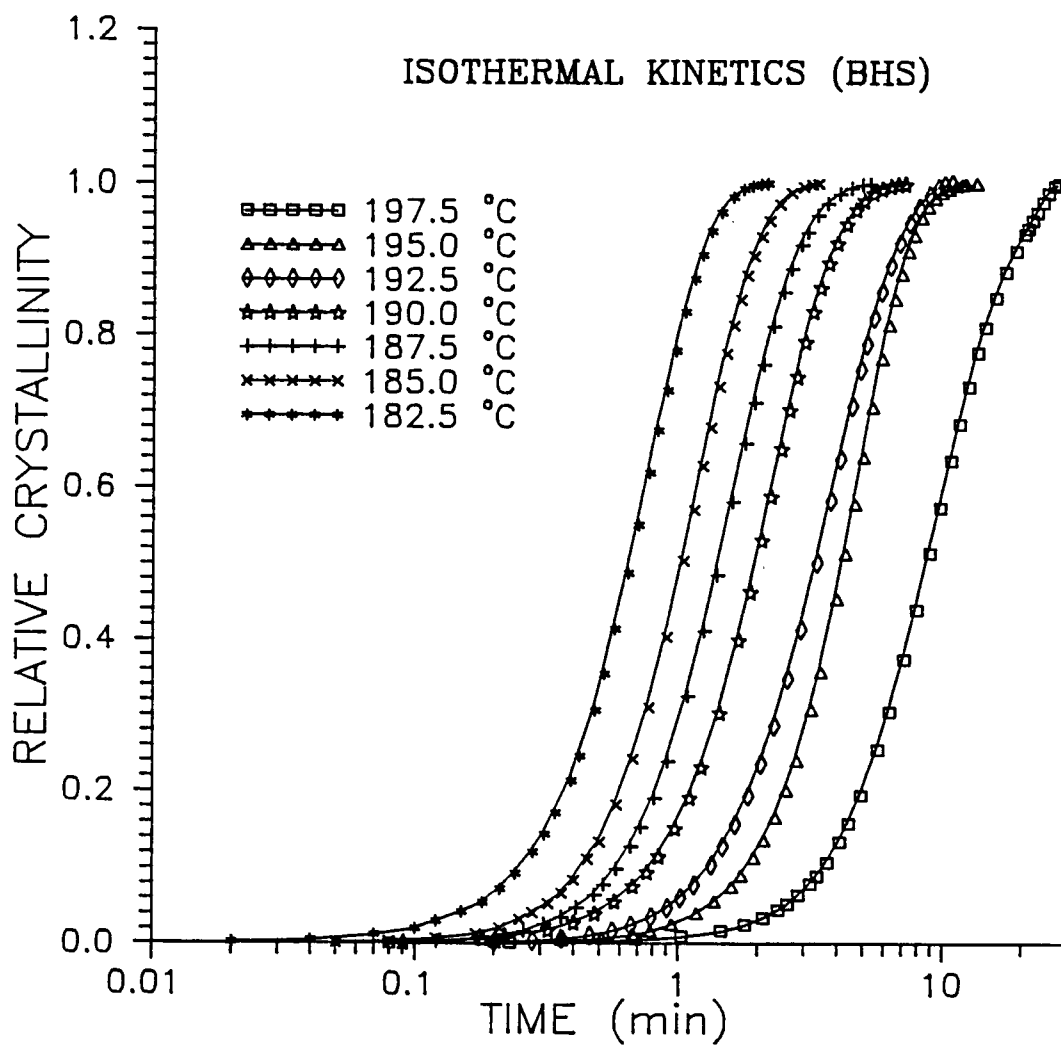


Figure 6.1. Isothermal crystallization kinetics data for BHS at various crystallization temperatures.

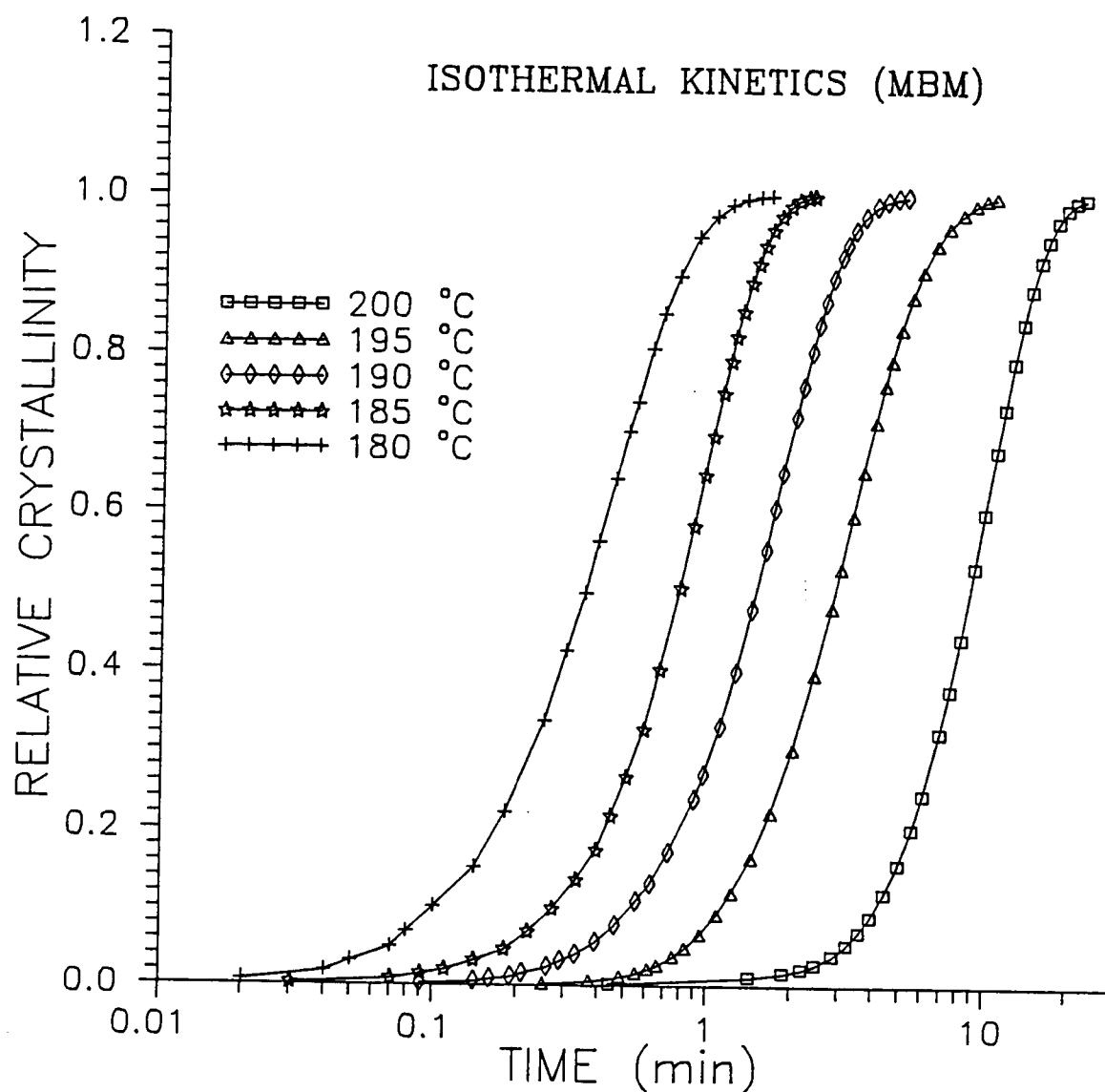


Figure 6.2. Isothermal crystallization kinetics data for MBM at various crystallization temperatures.

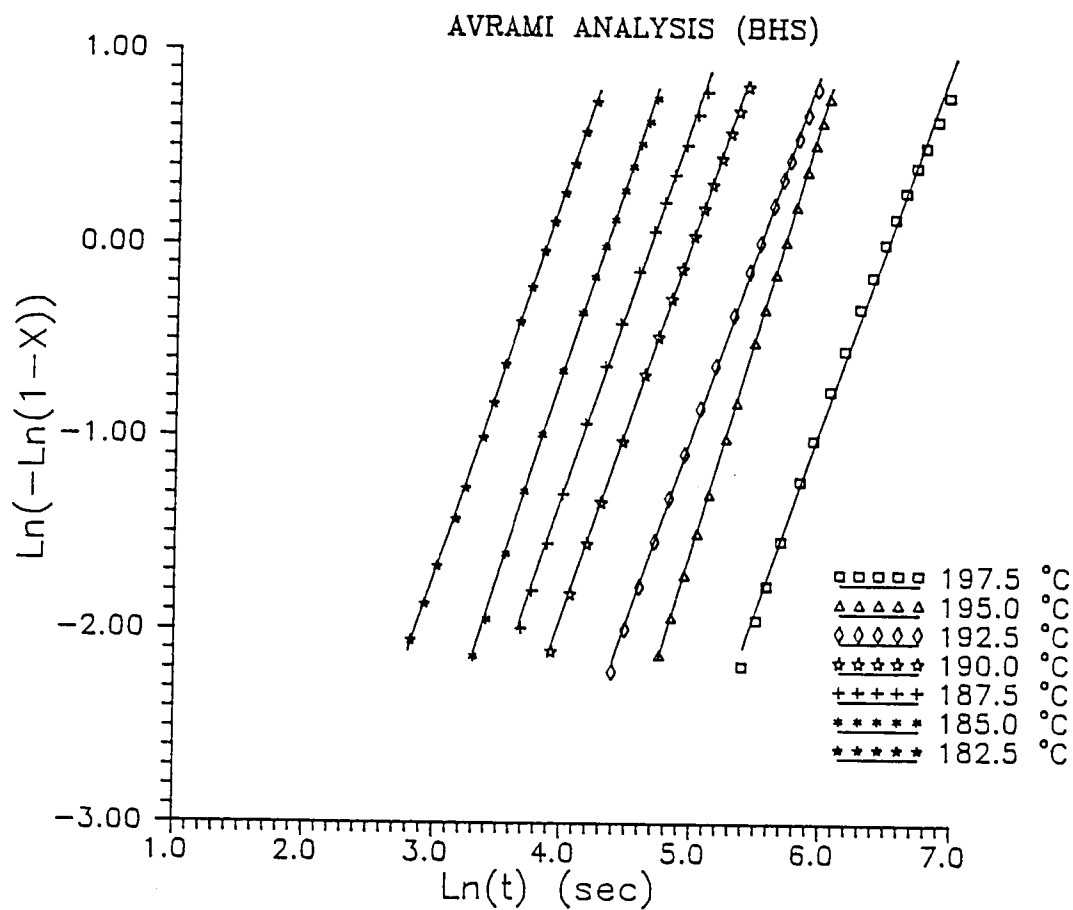


Figure 6.3. Avrami analysis of BHS isothermal crystallinity data.

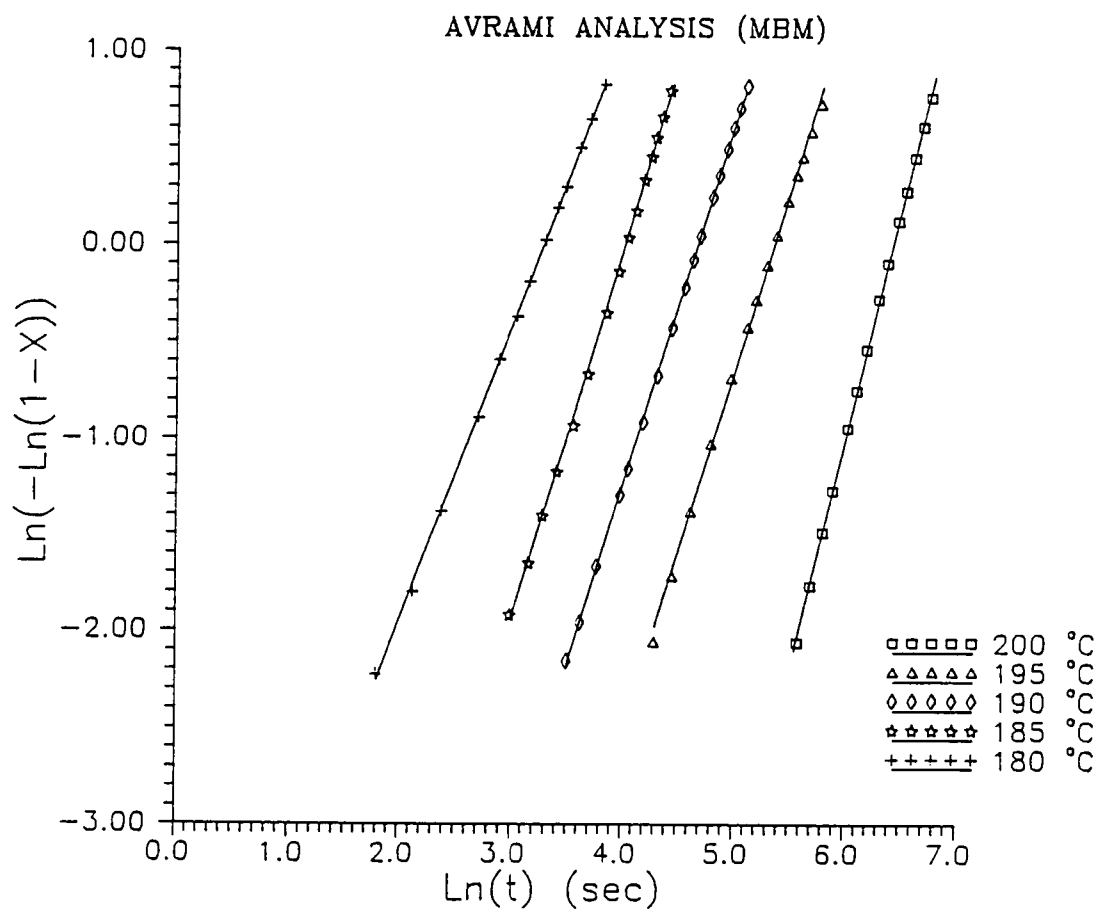


Figure 6.4. Avrami analysis of MBM isothermal crystallinity data.

temperature. The half-time values and Avrami indices for BHS and MBM-I resins are tabulated in Tables 5 and 6, respectively. The values of Avrami indices were found to be close to 2. This may be due to DSC being sensitive to the development of two-dimensional lamellae. As already noted, the half times could only be measured over a narrow range (180-200°C) of temperatures at low undercoolings. Thus, the experimentally obtained macroscopic rate of crystallization ($1/t_{1/2}$) needs to be extrapolated to lower temperatures (high supercoolings) where crystallization usually occurs in processing of semicrystalline polymers.

As noted in Chapter 2, the temperature variation of $t_{1/2}$ can be written using Hoffman-Lauritzen theory (refer Equation [2.4.10]). The plot of this half-time analysis for both BHS and MBM-I resins is shown as Figure 6.5. The glass transition temperature was taken to be 40°C and the equilibrium melting point was taken to be 260°C for the α form (139). U^* was taken to be 1500 cal/mole (61). The values of $(1/t_{1/2})_0$ and C_3 for BHS were found to be $1.107 \times 10^7 \text{ sec}^{-1}$ and $5.07 \times 10^5 (\text{°K})^2$, respectively. The values of $(1/t_{1/2})_0$ and C_3 for MBM-I were found to be $6.737 \times 10^6 \text{ sec}^{-1}$ and $4.804 \times 10^5 (\text{°K})^2$, respectively. The half times can then be extrapolated to lower temperatures and the Avrami rate constant k can then be calculated using $k = \ln(2)/(t_{1/2})^n$. The plot of extrapolated reciprocal half-times for BHS and MBM-I as a function of temperature is shown as Figure 6.6. The extrapolated half-time data from the literature (21) are also shown in Figure 6.6. It can be seen from Figure 6.6 that the literature values are significantly different at lower temperatures. It can also be seen from the Figure 6.6 that MBM-I has higher crystallization rates than BHS. This can be expected as resin with a lower average molecular weight tends to crystallize faster. Note that the literature reciprocal half times are significantly different at lower temperatures. Burnett and McDevit (140) have observed highest spherulite growth rate for nylon 6 at

Table 5 : Tabulation of half-times and Avrami indices at various crystallization temperatures for BHS resin

Temperature, °C	Half-time, sec	Avrami Index
197.5	525	1.92
195	252.3	2.27
192.5	201	1.94
190	118.6	1.99
187.5	86	2.0
185	62.2	2.09
182.5	39.4	2.0

Table 6 : Tabulation of half-times and Avrami indices at various crystallization temperatures for MBM-I resin

Temperature, °C	Half-time, sec	Avrami Index
200	529.2	2.38
195	171.6	1.87
190	88.2	1.86
185	46.5	1.91
180	21.0	1.53

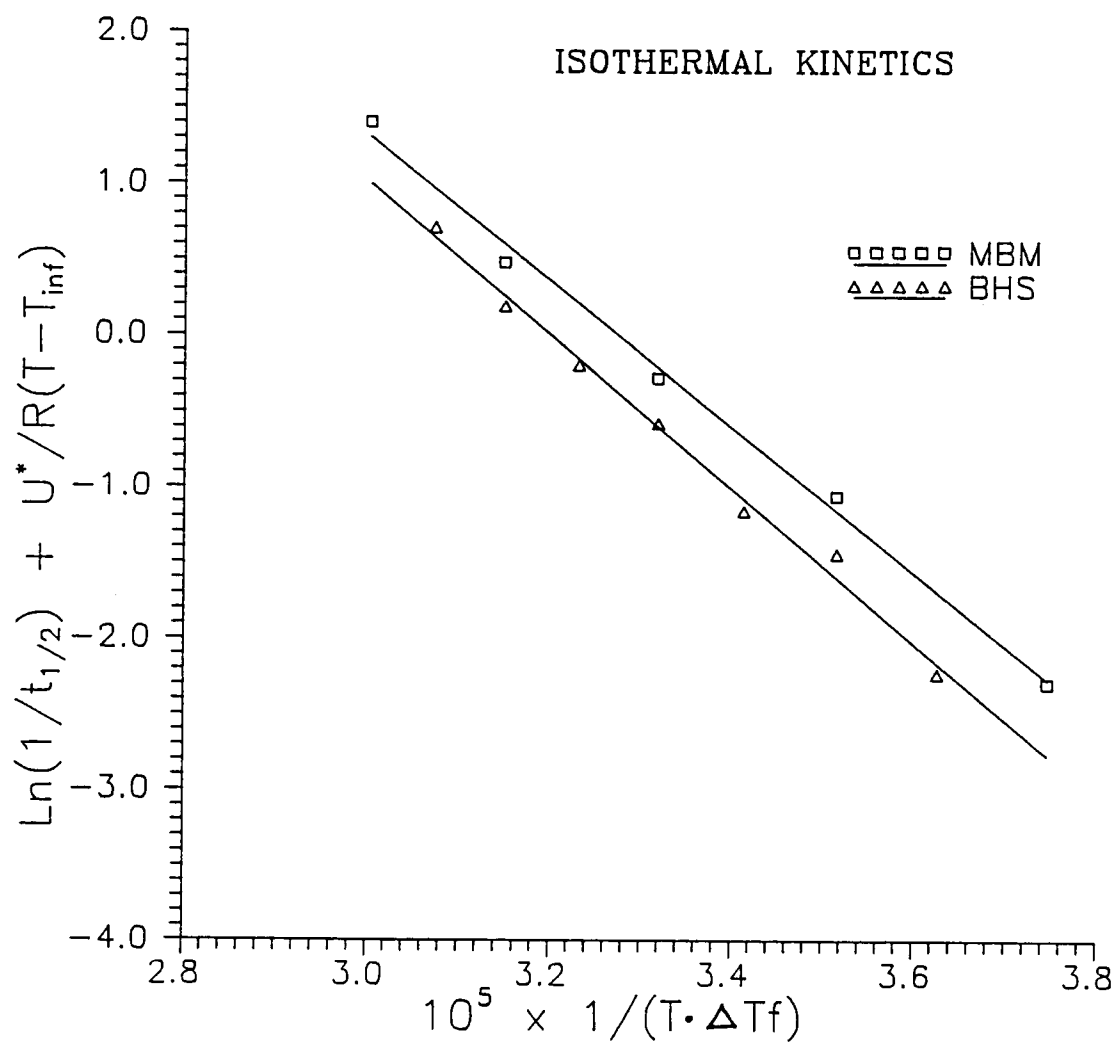


Figure 6.5. Plot of $\ln(1/t_{1/2}) + U^*/R(T-T_{\infty})$ versus $1/(T\Delta T_f)$ for BHS and MBM isothermal kinetics data.

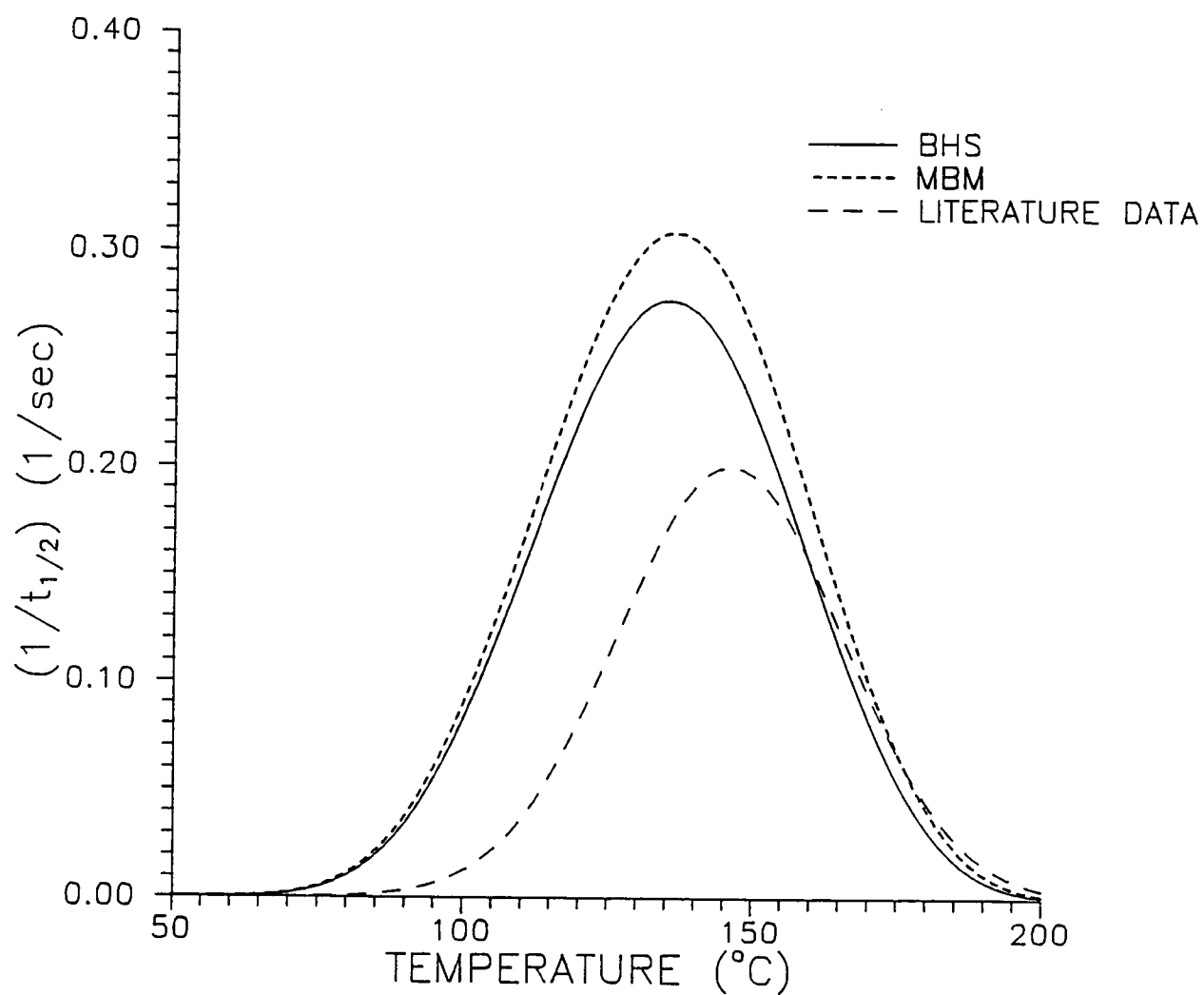


Figure 6.6. Plot of extrapolated half-times as a function of temperature. (—) is the data of BHS; (----) is the data of MBM; and (- - -) is nylon 6 half-time data from literature.

about 132 °C. Magill (141) has observed the highest spherulitic growth rate at about 138 °C and maximum crystallization rate ($1/t_{1/2}$) at about 140 °C for a nylon 6 resin using light depolarization microscopy technique. The extrapolated reciprocal half-time data on BHS and MBM-I showed maximum crystallization rate at about 135°C which is very close to the literature values. The half-time analysis approach is very useful to evaluate quiescent kinetics of a given resin. The utility of this approach has also recently been demonstrated and given extensive justification for polypropylenes (80). It must be mentioned, however, that very large extrapolations will be questionable using any procedure. This fact emphasizes the need to develop experimental techniques for studying crystallization rates at high undercoolings.

6.2 Quiescent Nonisothermal Kinetics

The description of crystallization in a spinline model requires that the non-isothermal, quiescent crystallization kinetics data obtained at low cooling rates are adequately described so that the results can be extrapolated into the cooling rate regime where crystallization takes place in the melt-spinning process. The nonisothermal crystallization kinetics data obtained for BHS and MBM-I resins using DSC are shown in Figures 6.7 and 6.8, respectively. As already noted, the maximum cooling rate available using DSC was only 40 °C/min. It can be seen from Figures 6.7 and 6.8 that the MBM-I resin crystallized at higher temperatures than BHS resin at all cooling rates. This is to be expected as MBM-I resin had higher isothermal rates than BHS resin. It can also be noted that, the higher the cooling rate, the lower is the temperature at which the crystallization begins for both the resins.

As noted in Chapter 2, the general Avrami theory of phase change can be extended so as to describe nonisothermal crystallization kinetics. However, the general

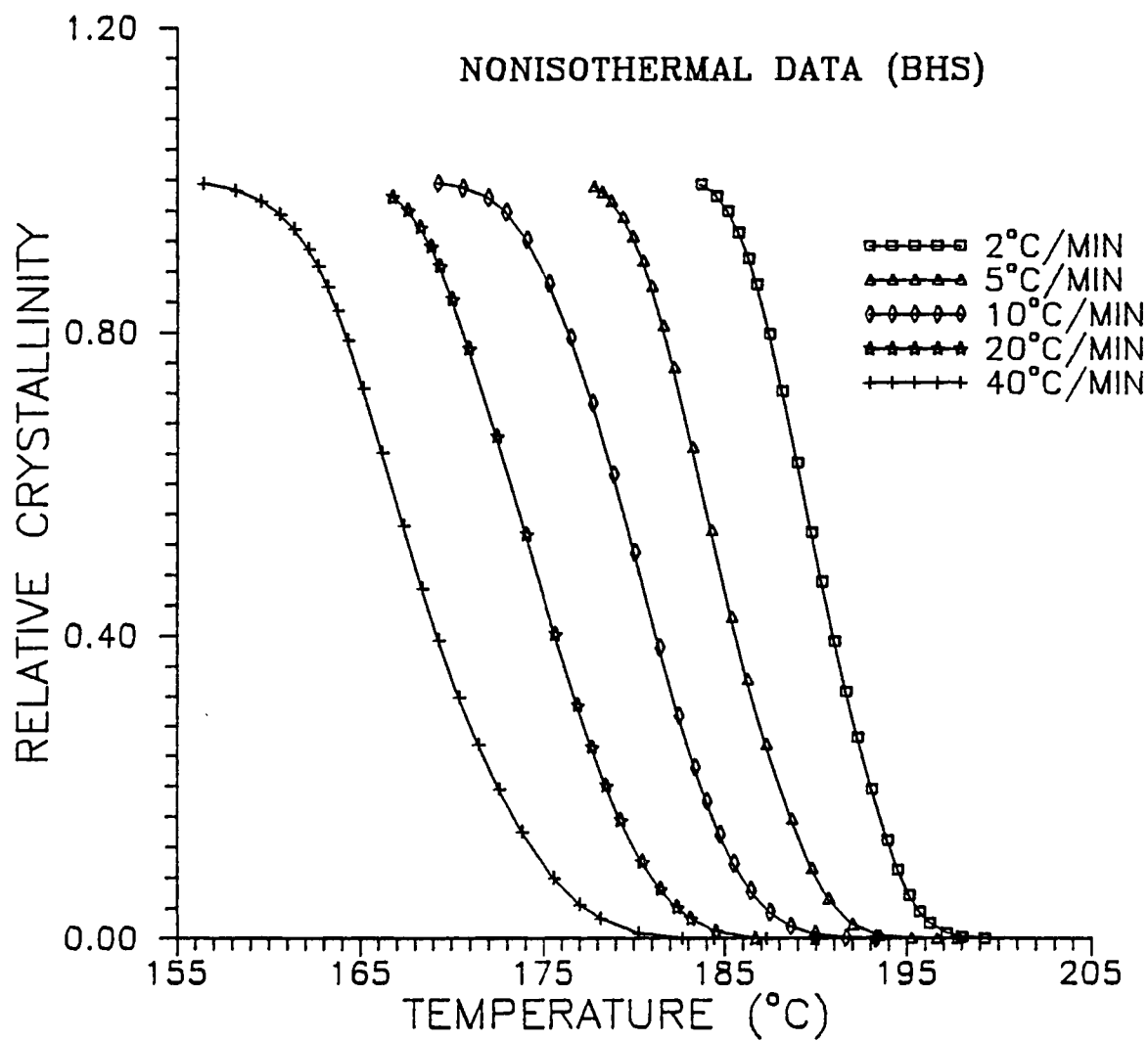


Figure 6.7. Nonisothermal crystallization data of BHS resin.

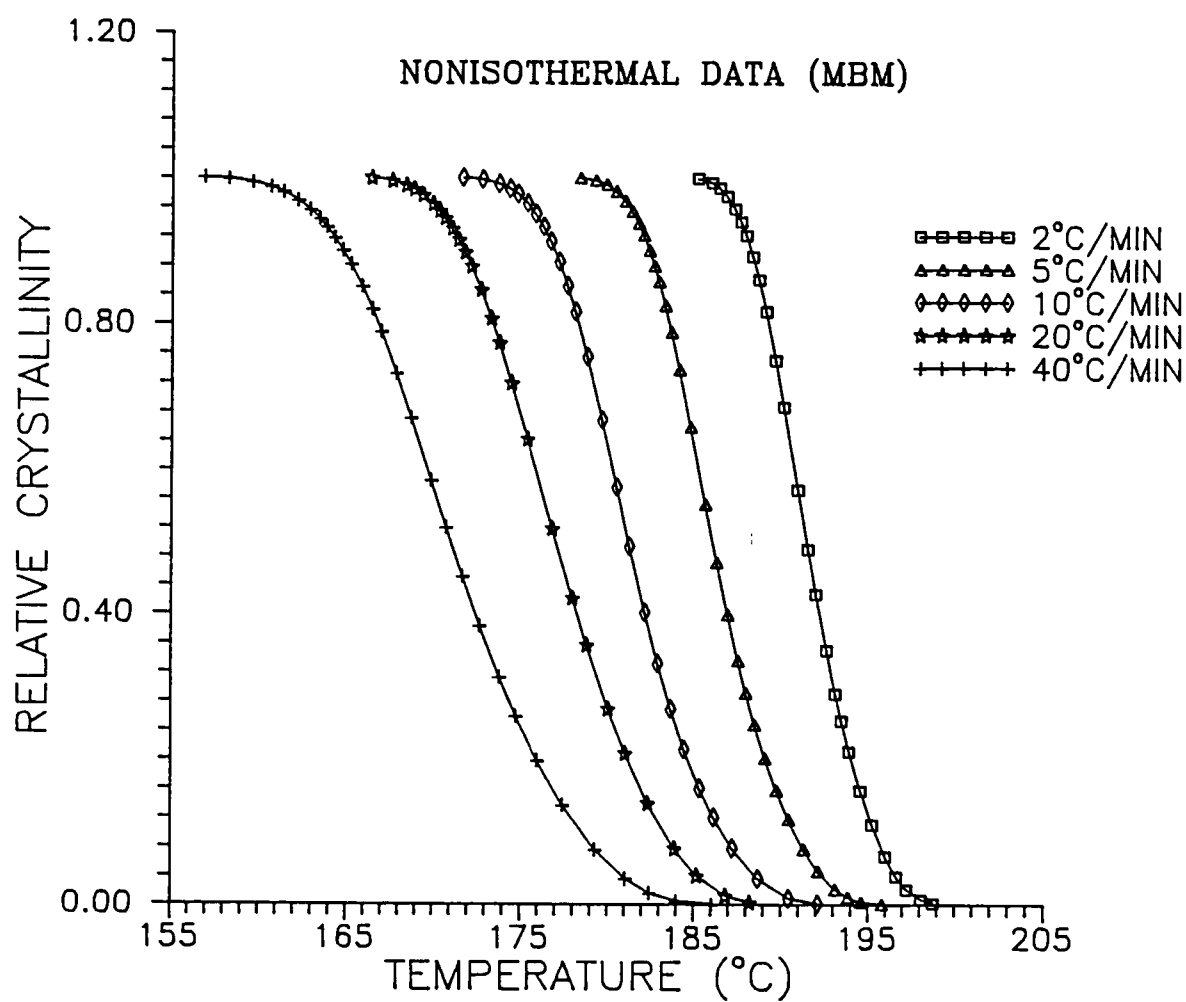


Figure 6.8. Nonisothermal crystallization data of MBM resin.

nonisothermal theory (refer to Equation [2.4.11]) is usually simplified to obtain more tractable models to deal with nonisothermal crystallization.

Using the simplifying assumption of constant cooling rate, Ozawa has extended the Avrami equation to describe nonisothermal crystallization (refer to Equation [2.4.12]). The Ozawa analysis of BHS and MBM-I nonisothermal crystallization data is shown in Figures 6.9 and 6.10, respectively. It can be noted that the Ozawa analysis does describe nonisothermal data of BHS and MBM-I resins. The values of Ozawa exponent at various temperatures for both the resins are tabulated in Table 7.

It can be observed that the Ozawa analysis requires values of relative crystallinity at a given temperature for different cooling rates. Hence, it can be observed from Figures 6.7 and 6.8 that it is not possible to include a wide range of cooling rates and the temperature range over which the analysis can be applied is very narrow. Also, the Ozawa analysis is hardly of any value for modeling the development of crystallinity in polymer processing mainly because it assumes constant cooling rate.

The predictions of nonisothermal crystallization from isothermal data using the Kamal model (refer to Equation [2.4.15b]) are compared with the nonisothermal experimental data for BHS in Figure 6.11. The integral was computed from $T_0=250\text{ }^{\circ}\text{C}$ (solid lines) and $T_0=210\text{ }^{\circ}\text{C}$ (dashed lines). Note that nonisothermal crystallization occurred over a temperature range close to that in which the isothermal rates were measured. Hence, a minimal extrapolation of half-times was required. Similar predictions for the Nakamura Model (refer to Equation [2.4.13b]) for BHS are shown in Figure 6.12. Avrami index $n=2$ was used in both models. It can be observed from Figures 6.11 and 6.12 that both models in their integral form overpredict the nonisothermal crystallinity data. However, the integral Nakamura model gave far better predictions than the integral Kamal model. The integral Kamal model substantially

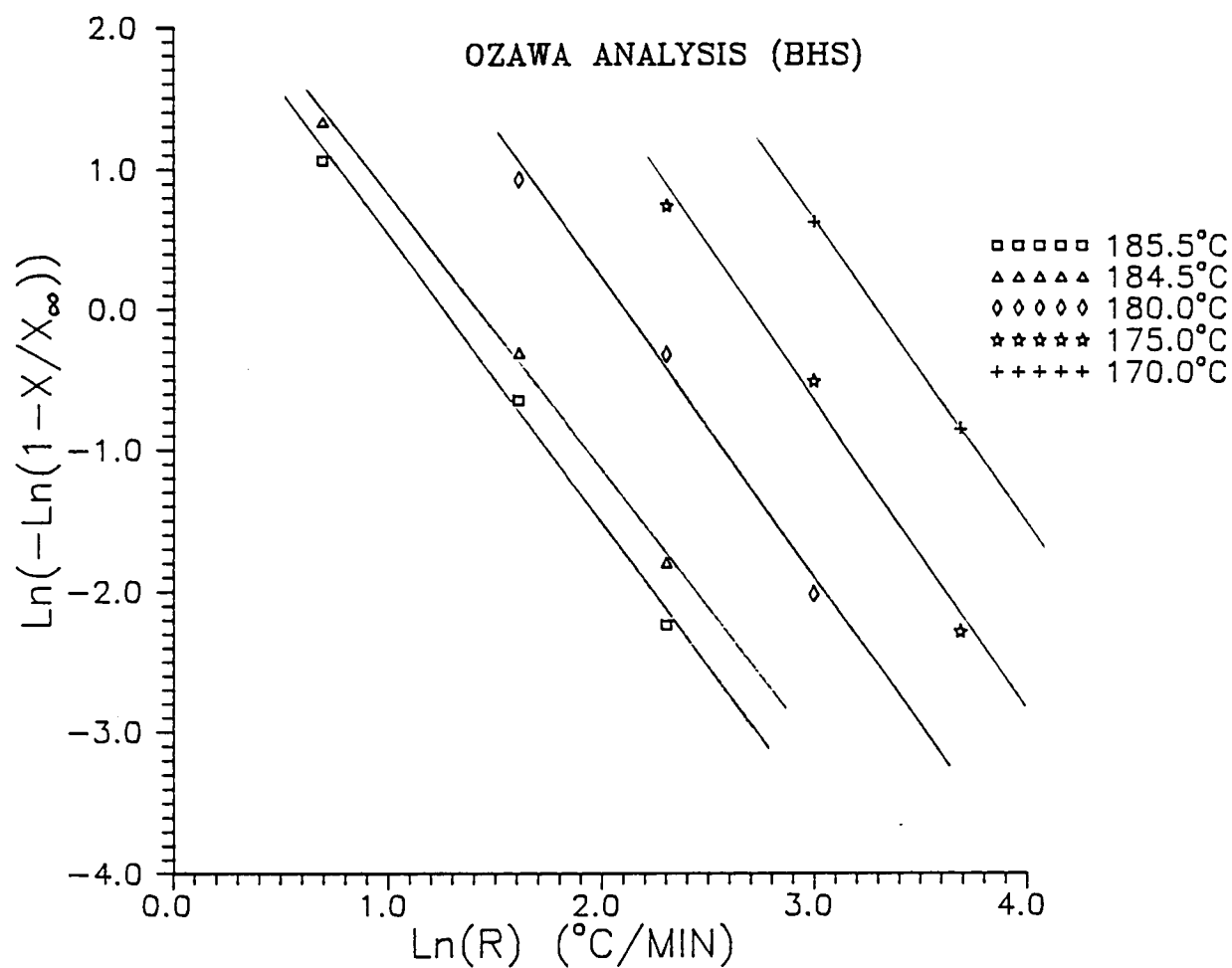


Figure 6.9. Ozawa analysis of BHS nonisothermal crystallization data.

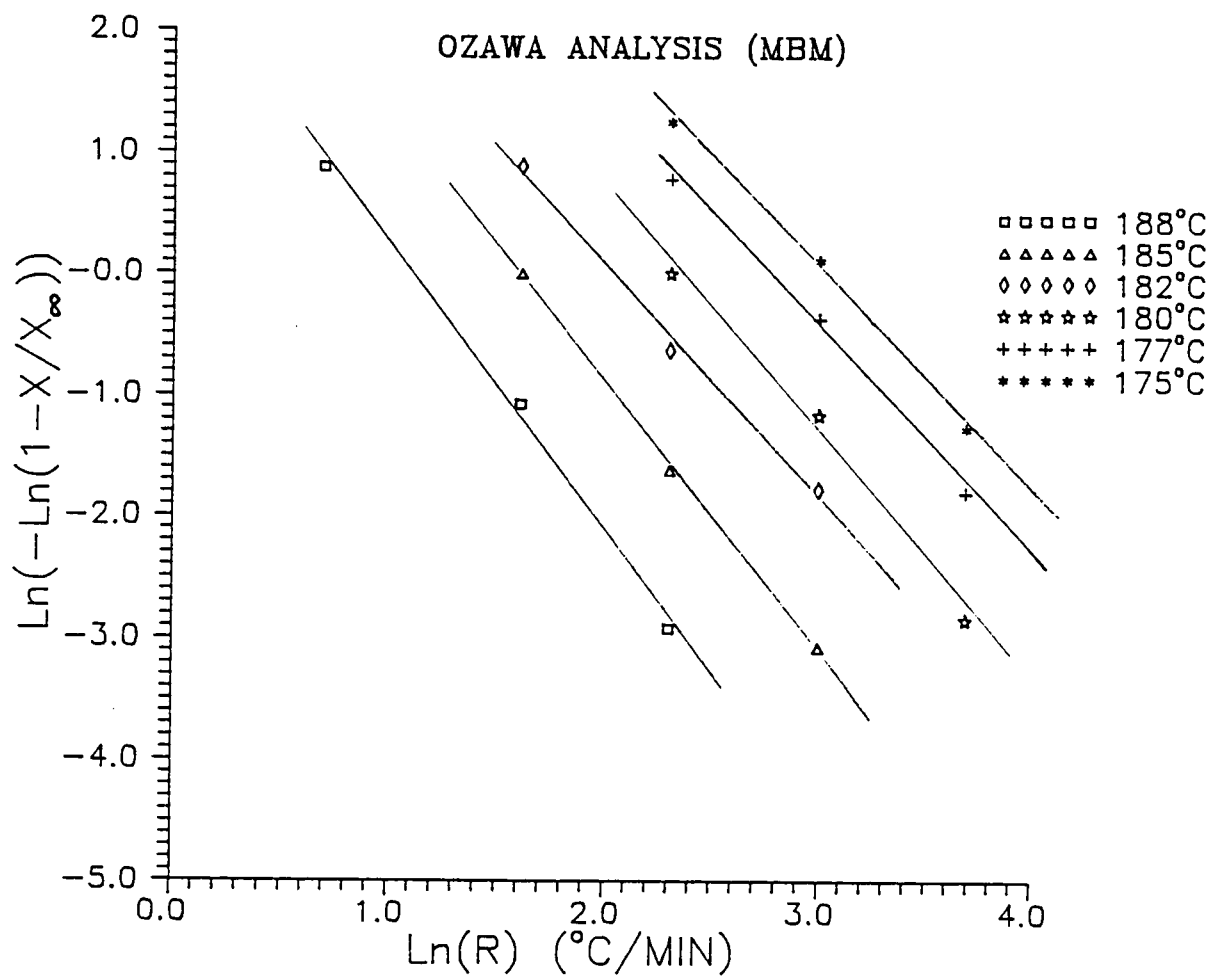


Figure 6.10. Ozawa analysis of MBM nonisothermal crystallization data.

Table 7 : Values of Ozawa exponent at various temperatures for BHS and MBM-I resins.

BHS Resin		MBM-I resin	
Temperature °C	n	Temperature °C	n
187	2.31	187	2.28
185.5	2.04	185	2.21
184.5	1.94	184	2.08
183	1.97	183	1.99
182	2.37	182	1.92
180	2.12	180	2.05
177	2.49	177	1.87
175	2.18	175	1.82
173	1.99	173	1.97

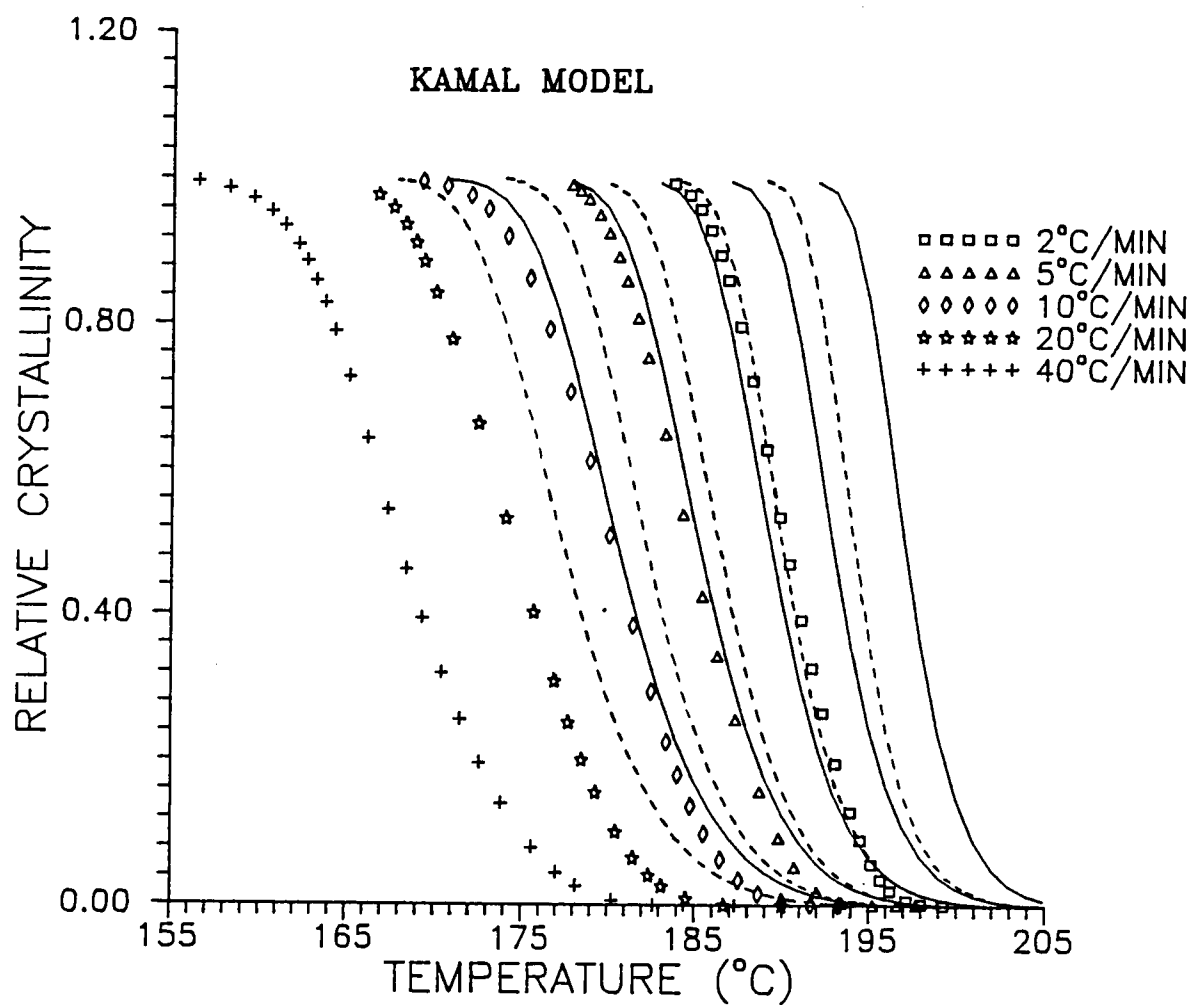


Figure 6.11. Comparison of experimental and predicted nonisothermal crystallinity data of BHS using the integral Kamal model at different cooling rates. Solid lines are predictions using $T_0=250$ °C and dashed lines are predictions using $T_0=210$ °C.

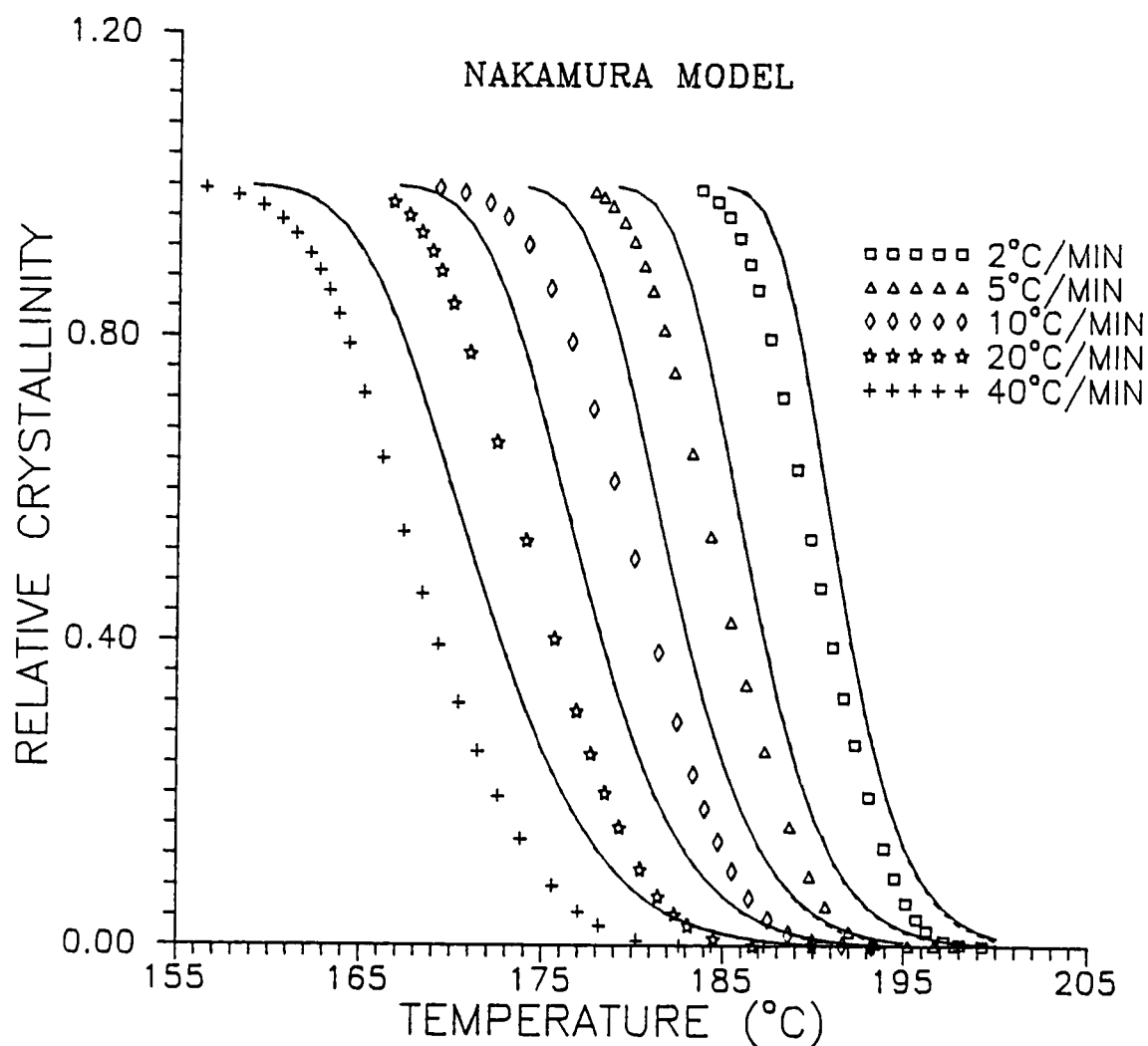


Figure 6.12. Comparison of experimental and predicted nonisothermal crystallinity data of BHS using the integral Nakamura model at different cooling rates. Solid lines are predictions using $T_0=250$ °C and dashed lines are predictions using $T_0=210$ °C.

overpredicts the nonisothermal data. In fact, for the Kamal model the predictions depend very much on the temperature from which one starts computing the integral (i.e. from when the residence time t is computed) as can be observed in Figure 6.11. This is because the value of the integral in equations [2.4.15a] or [2.4.15b] would depend on when one starts counting residence time, t . The Kamal model also has a problem of when to start counting residence time (which is difficult to estimate) in a polymer processing operation. The differential Kamal model also has a dubious functional form in which the rate of crystallization depends explicitly on residence time apart from temperature and crystallinity (refer to Equation [2.4.16] without the exponential factor).

For the integral Nakamura model, the predictions were insensitive to T_0 values in the range 250 °C-210 °C (which includes melting temperature of nylon 6) as shown in Figure 6.12. This is to be expected as the Nakamura model does not contain time as an explicit variable. The differential Nakamura model also has an intuitively more satisfactory functional form in which the rate of crystallization depends only on temperature and crystallinity (refer to Equation [2.4.14]). Similar functional form for a differential rate equation was also assumed by Malkin, et al. (151) in their general treatment of polymer crystallization kinetics. For these reasons, the Nakamura model is superior for predicting the development of crystallization in process modeling. For the differential Nakamura model the numerical requirement of a non-zero initial crystallinity condition can be circumvented by keeping initial crystallinity very close to zero (for example, $\theta_0=10^{-15}$). This may be because nuclei of the new phase may, generally speaking, be present (or form instantaneously in a spontaneous manner) in the melt. This possibility is not taken into account in the general Avrami equation [2.4.11] or in the Nakamura model (151). A differential form of Kamal model would not be as satisfactory

for predicting development of crystallinity in polymer processing as it involves the calculation of residence time of a material particle which normally is difficult and ambiguous to evaluate and the functional form also appears to be fundamentally incorrect.

The Nakamura model, both in the integral and the differential form (with $T_0 > 210^\circ\text{C}$), overpredicts the nonisothermal data on BHS primarily because the Nakamura model does not account for the induction (lag) time for nucleation. To eliminate the induction time effects, the lowest measurable crystallinity value using DSC at corresponding temperature (which would be different for different cooling rate) was used as an initial condition in the differential form of the Nakamura model (refer to Equation [2.4.14]). The predictions are compared with the nonisothermal data for BHS and MBM-I in Figures 6.13 and 6.14, respectively. It can be observed from Figures 6.13 and 6.14 that the differential Nakamura model with the above mentioned initial condition marginally overpredicts the nonisothermal data. This is probably due to simultaneous annealing in isothermal crystallization which leads to higher crystallinities and lower half-times. These values when used in the Nakamura model would marginally overpredict the development of crystallinity under nonisothermal conditions as annealing is minimal under dynamic cooling crystallization.

As noted in Chapter 2, some investigators have used non-linear regression methods to fit nonisothermal data directly (76,78). Using a simpler approach, the nonisothermal crystallization data for BHS and MBM-I are directly fitted here using the differential form of Nakamura model (equation [2.4.14]) using the Marquart Algorithm (142). Marquart Algorithm is based on an interpolation technique between the Gauss-Newton and the Steepest-descent methods. The nonlinear regression program provided by Constantinides (142) has been designed to fit a set of differential or algebraic

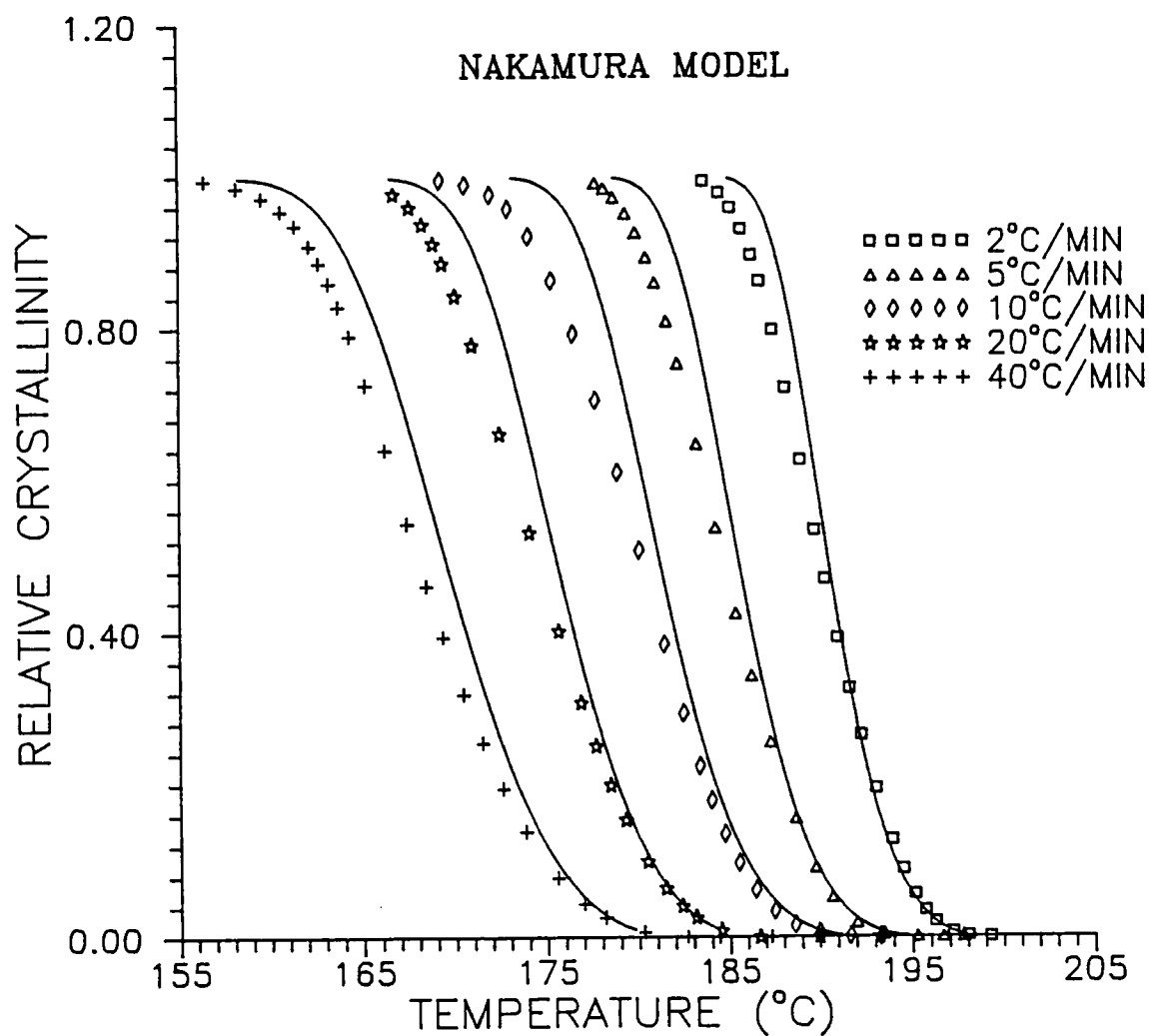


Figure 6.13. Comparison of experimental and predicted nonisothermal crystallinity data of BHS using the differential form of the Nakamura model at different cooling rates.

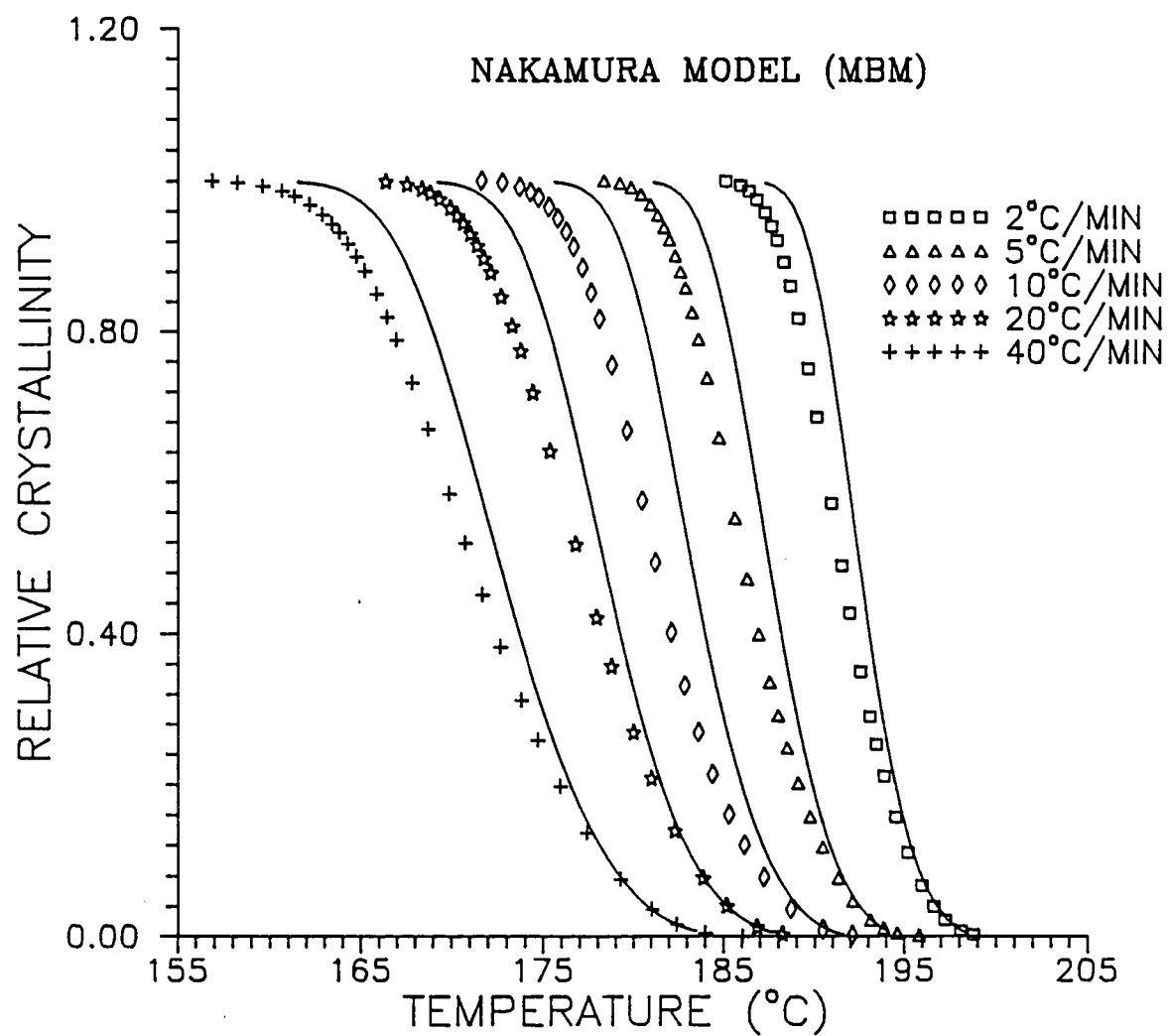


Figure 6.14. Comparison of experimental and predicted nonisothermal crystallinity data of MBM using the differential form of the Nakamura model at different cooling rates.

equations to multiresponse data to determine a number of unknown parameters. The parameter estimation is linked with statistical analysis routines to form a single self-contained package. If the model equations are differential equations, then the variational equations must be developed. These are obtained by taking the partial of the differential equations with respect to the parameters. The convergence in the program can be based upon either regular sum of squared residuals or sum of normalized squared residuals. The program description is given in detail in reference (142). However, the original program was written in interpreted BASIC (BASICA in IBM PC) and was very slow to run. Hence, the program was modified by the author so that it can be run using compiled BASIC. The program was also modified to read external data files of nonisothermal crystallinity data. In a non-linear regression method, the best values of N number of parameters are searched over a large region of N-dimensional space so as to find the global minimum in the sum of the squares of errors. However, equation [2.4.14] suffers from the disadvantage that for certain values of parameters $(1/t_{1/2})_0$ and C_3 , the equation would predict θ to be greater than one and this would result in the logarithm of a negative number. Letting $Y = \ln[1/(1-\theta)]$ simplified the differential equation [2.4.14] and eliminated this problem. Note that $0 < \theta < 1$ corresponds to $0 < Y < \infty$. For fitting crystallinity data up to 95 percent relative crystallinity, Y would vary from 0 to 3. Note that $K = k^{1/n} = (\ln 2)^{1/n} / (1/t_{1/2})_0$. Hence, using Equation [2.4.14], we get the following expression:

$$\frac{dY}{dt} = n K (Y)^{\frac{n-1}{n}} \quad [6.2.1]$$

$$\text{where } K = (\ln 2)^{\frac{1}{n}} \left(\frac{1}{t_{1/2}} \right)_0 \exp \left[- \frac{U^*}{R(T - T_\infty)} \right] \exp \left[- \frac{C_3}{T \Delta T f} \right]$$

Denoting $K_0 = (\ln 2)^{1/n} (1/t_{1/2})_0$, the nonisothermal data can be fitted using K_0 , C_3 and Avrami index n as parameters of the model [6.2.1]. However, for each parameter, a variational equation has to be obtained by taking partial derivative of the model equation [6.2.1] with respect to that parameter. For the nonlinear regression fitting of equation [6.2.1], the sum of normalized squared residuals was selected for the convergence criterion. Avrami index (n) decides the shape of the sigmoidal nonisothermal crystallinity curve. Hence, n can be fixed to a value which would predict the correct shape of the sigmoidal curve, thereby giving lowest possible sum of normalized squared residual. The Avrami index $n=2$ was found to predict correct shape of the nonisothermal crystallinity curve. However, keeping $n=2$, nonisothermal data could be equally well fitted with various pairs of values of $(1/t_{1/2})_0$ and C_3 . Hence, the value of C_3 was subsequently kept constant while solving for the value of K_0 . This was repeated for three values of C_3 equal to 4×10^5 , 5×10^5 , and 6×10^5 . The data for each cooling rate was fitted individually to obtain a K_0 value for a given C_3 value. The K_0 values at each cooling rate for these values of C_3 are tabulated in Table 8 for BHS data. It can be seen from Table 8 that the values of K_0 are almost constant at different cooling rate for $C_3=5 \times 10^5$ as desired. Note that this value of C_3 is very close to that obtained from isothermal half-time analysis. However, for $C_3=4 \times 10^5$, the value of K_0 increased with an increase in cooling rate. For $C_3=6 \times 10^5$, the value of K_0 decreased with an increase in cooling rate. These results suggest that the value of $C_3=5 \times 10^5$, as found from the isothermal data, is also the most appropriate value for describing the nonisothermal results of BHS. Similar results were obtained for MBM-I resin. The average of K_0 values for $C_3=5 \times 10^5$ for BHS and MBM-I resins were equal to 6.134×10^6 and 7.8×10^6 respectively. Note that the K_0 value for MBM-I is higher than that for BHS as

Table 8 : Tabulation of K_o values for various C_3 values for BHS at different cooling rates obtained using Equation [6.2.1]

$^{\circ}\text{C}/\text{min}$	$C_3 = 4 \times 10^5$	$C_3 = 5 \times 10^5$	$C_3 = 6 \times 10^5$
2	2.08×10^5	6.37×10^6	1.863×10^8
5	2.14×10^5	5.94×10^6	1.517×10^8
10	2.42×10^5	5.83×10^6	1.303×10^8
20	3.22×10^5	6.22×10^6	1.163×10^8
40	3.70×10^5	6.30×10^6	1.046×10^8

expected since MBM-I crystallizes faster than BHS. The differential Nakamura model predictions using these average values of K_O and $C_3=5 \times 10^5$ for BHS and MBM-I are compared with the experimental data at different cooling rates in Figures 6.15 and 6.16, respectively. The predictions match the experimental data very well. However, the integral Nakamura model still gave marginal overprediction. It is important to note that using this procedure, the nonisothermal data at cooling rates from 2 to 40 °C/min could be fitted with single value of parameters C_3 and $(1/t_{1/2})_0$ as would be desired. This in itself justifies using a single value of C_3 to predict nonisothermal data at cooling rates higher than 2 °C/min. It can also be noted that crystallization at cooling rates higher than 2 °C/min would occur at higher supercoolings, probably corresponding to Regime III in Hoffman's regime analysis. This non-linear regression procedure can be directly used to fit nonisothermal data to obtain K_O and C_3 values without isothermal measurements. The same values of the parameters can then be used to predict the quiescent nonisothermal data at higher cooling rates. This approach is of significant value for modeling nonisothermal processes and for comparing stress-induced crystallization results, e.g. obtained in a spinline, with the quiescent nonisothermal results.

Finally, it is interesting to note that a phenomenological derivation of the Nakamura model can be obtained as follows. Noting that the functional form for nonisothermal crystallization should be of the form $d\theta/dt = K(T) g(\theta)$ (28), an appropriate $g(\theta)$ needs to be obtained. One choice for $g(\theta)$ can be obtained noting the differential form of isothermal Avrami expression

$$\frac{d\theta}{dt} = n k^{\frac{1}{n}} (1-\theta) \left[\ln \left(\frac{1}{1-\theta} \right) \right]^{\frac{n-1}{n}} \quad [6.2.2]$$

Hence, choosing $g(\theta) = n (1-\theta) [\ln(1/1-\theta)]^{(n-1)/n}$ (or substituting $K(T)=k^{1/n}$ in Equation

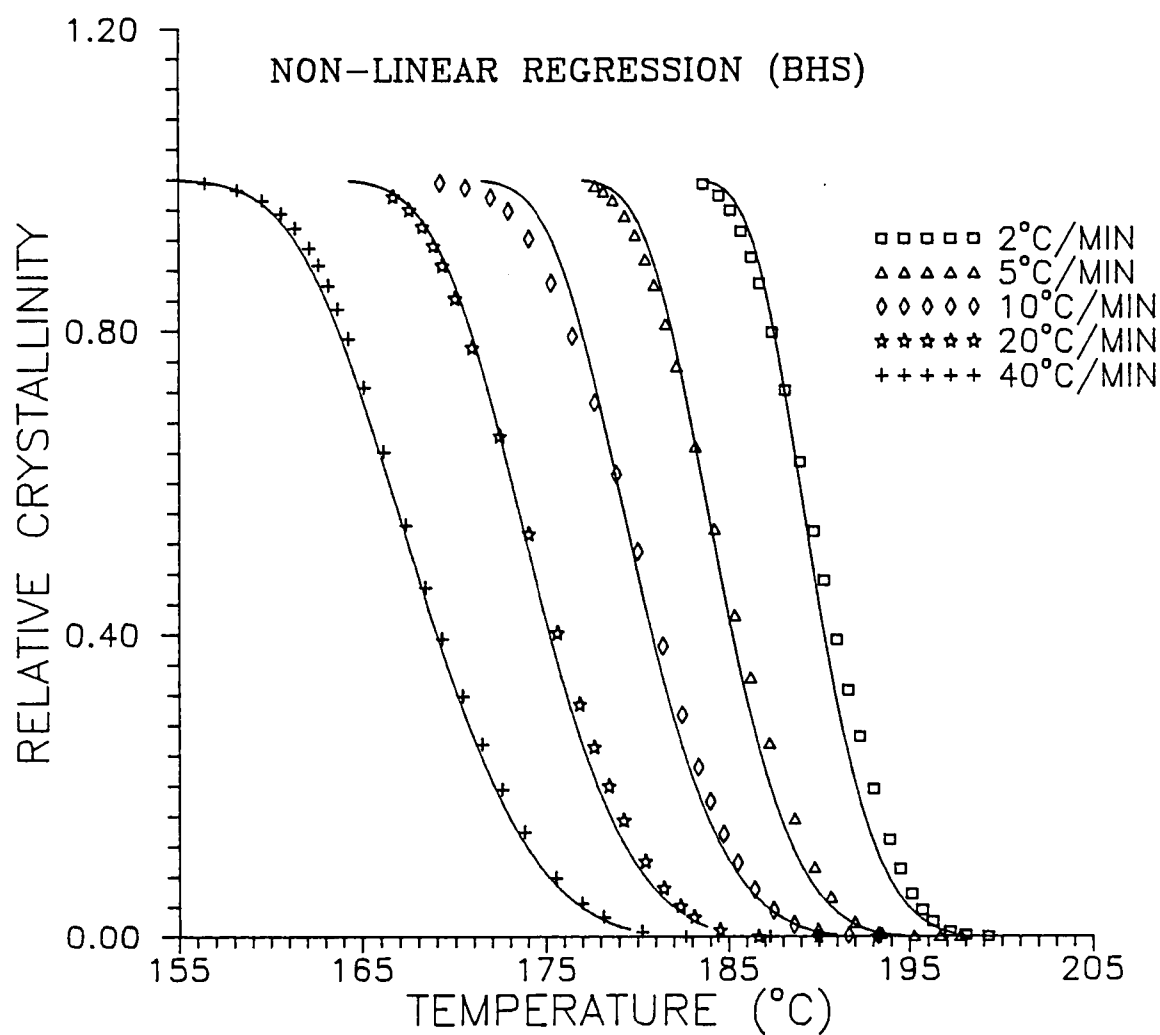


Figure 6.15. Non-linear regression fitting of the nonisothermal crystallization data of BHS using the differential form of the Nakamura model.

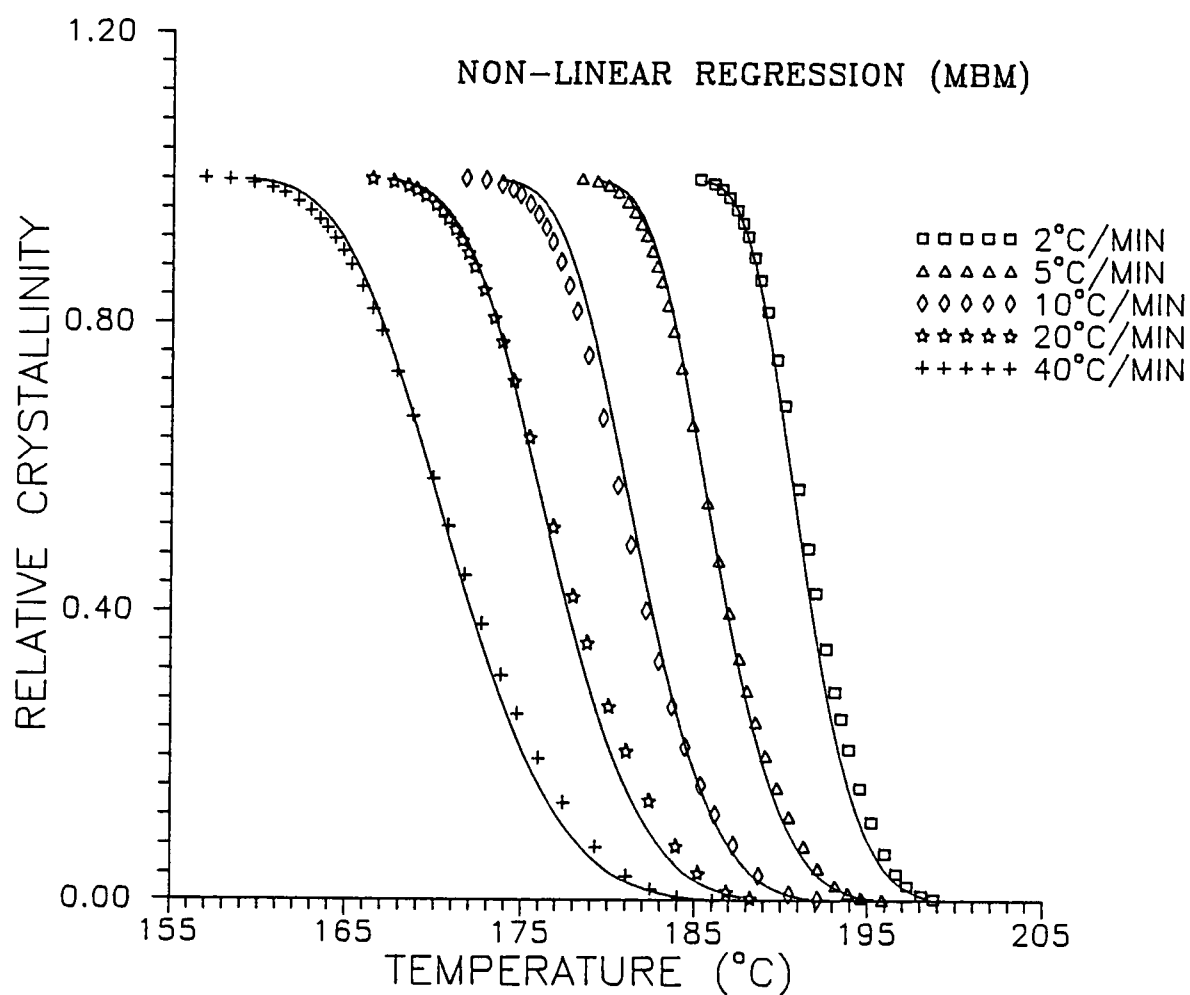


Figure 6.16. Non-linear regression fitting of the nonisothermal crystallization data of MBM using the differential form of the Nakamura model.

[6.2.2]), the differential form of the Nakamura model is obtained. Using the substitution $Y = \ln[1/(1-\theta)]$, one can easily integrate the differential equation to obtain the integral Nakamura model.

6.3 Orientation Effects in Melt Spinning

In addition to the thermal conditions, polymer crystallization is very sensitive to molecular orientation in the amorphous regions. Ziabicki (21) has presented a phenomenological analysis of orientation dependence of crystallization rate and has proposed that $k(T, f_a) = k(T) \exp(A(T)f_a^2)$. Here, f_a is the average Hermans orientation factor for the amorphous phase. The parameter $A(T)$ can be determined from independent experiments (109) or it can be estimated from melt spinning data (17,149).

Following Katayama and Yoon (16), Patel and Spruiell (149) have proposed an extension of half-time analysis to include orientation effects:

$$\left(\frac{1}{t_{1/2}}\right) = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{C_3}{T\Delta T f + CT^2 f_a^2}\right] \quad [6.3.1]$$

The above mentioned empirical equations neglect the orientation distribution of amorphous segments and the effects of "selective" orientation-dependent crystallization on the orientation distribution of remaining amorphous segments. However, they are still useful in semi-quantitative analysis of orientation-induced crystallization.

The quiescent kinetics data of BHS resin can now be used in the spinline model using the proposed extension of half-time analysis. However, the spinline model based on equation [6.3.1] could not quantitatively predict the spinline crystallization at the

highest take-up speed (6660 m/min) for the range of C values (0-500) tried. In fact, it predicted on-line crystallization at lower speeds where no crystallization was actually observed on the spinline for C values partially matching the data at the highest speed. The failure of extended half-time analysis to predict nylon 6 on-line crystallization may be due to failure of nucleation rate theory (so-called "nucleative collapse") at combinations of high stresses and supercoolings as mentioned by George (150) and discussed below. The mechanism for crystallization then changes from a nucleation and growth process to a virtually homogeneous transformation throughout the material. The rate of this transformation is much more rapid than nucleated growth.

It can be seen from equation [6.3.1] that the the right-most exponential term will always be less than unity. Assuming that it's value is unity, one can calculate maximum possible crystallization rate at any temperature. Using $K_0=6.134 \times 10^6$ and $C_3=5 \times 10^5$ for BHS, one obtains, e.g., $k_{\max} = 3,230 \text{ sec}^{-1}$ at 110°C , $k_{\max} = 11,367 \text{ sec}^{-1}$ at 130°C . From the data of BHS at the spinning speed of 6660 m/min (4,5), it can be seen that crystallization was triggered at about 120°C and crystallization rates of the order of $10,000 \text{ sec}^{-1}$ were obtained on spinline. Thus, maximum possible crystallization rates from nucleation rate theory barely approach the spinline crystallization rates.

However, the nylon 6 spinline crystallization was adequately described by the Ziabicki modification term $\exp(Af_a^2)$ as shown before with quiescent kinetics data taken from the literature (21). The Ziabicki term also semi-quantitatively described nylon 6 (BHS) on spinline crystallization using measured quiescent rates on BHS and the same value of $A=225$. This is shown in Figure 6.17 where the measured birefringence profiles for BHS at various speeds are compared with the model predictions. The higher birefringence values predicted for the highest take-up speed may partially be due to higher

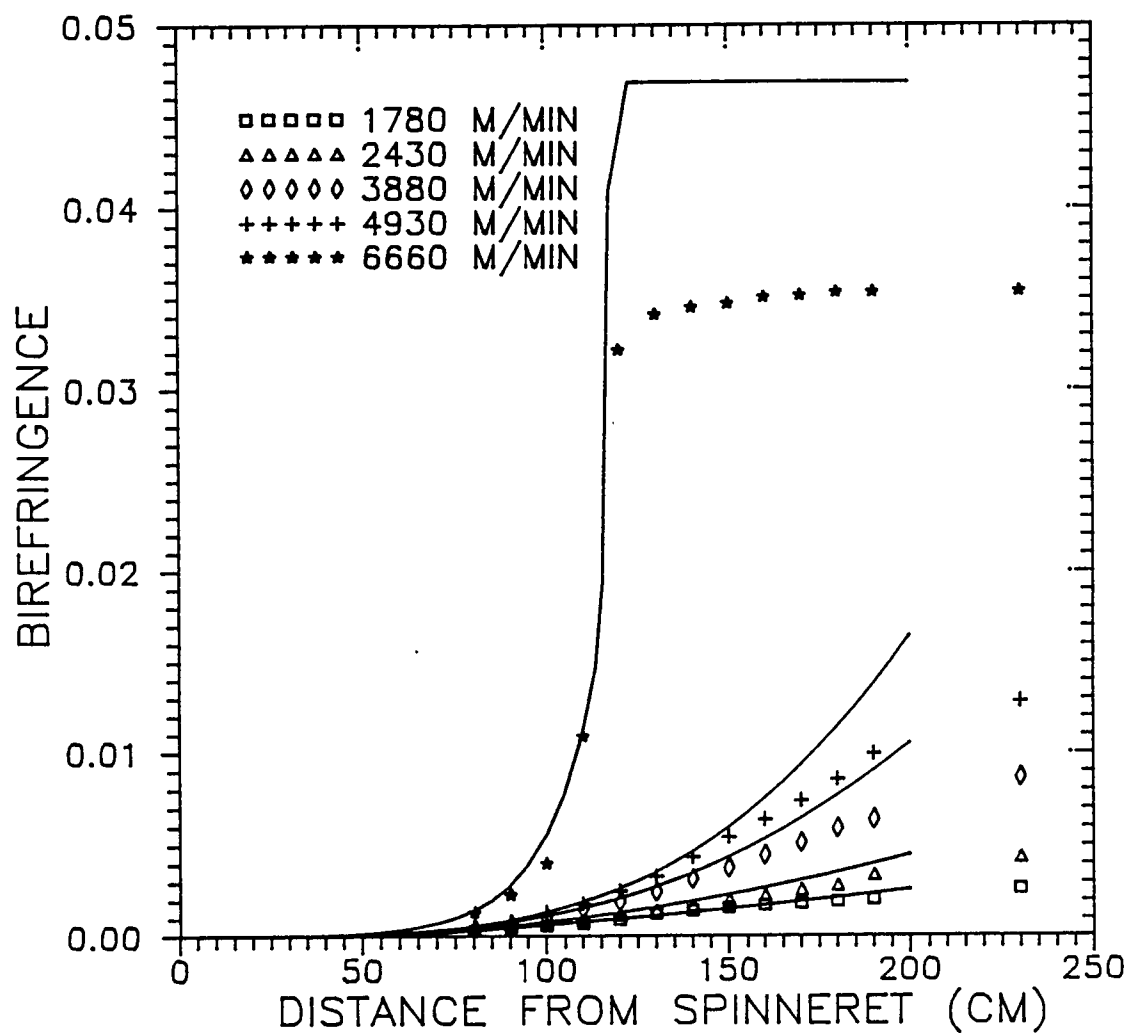


Figure 6.17. comparison of the spinline model predictions using measured quiescent kinetics data with the on-line birefringence measurements for BHS resin melt spun with a mass throughput of 2.993 m/min.

assumed values of crystalline birefringence contribution. The Avrami index $n=1$ was used in the calculations. Different values of index n do not affect the calculations appreciably (149).

It should be noted, however, that the extended half-time analysis may be a valid approach for describing stress-induced crystallization for fast crystallizing polymers such as polypropylene at low stresses. In this case, what is needed is a functional form that modifies the quiescent rates when orientation is present and reduces to the standard half-time analysis for quiescent crystallization. Equation [6.3.1] has the advantage that it can be justified on the basis of theory so long as nucleation and growth concepts remain valid.

CHAPTER 7

BASIC RHEOLOGICAL AND MELT SPINNING STUDIES OF BHS, LSB AND MBM RESINS

7.1 Basic Rheological Measurements

A cone-and-plate apparatus (Rheometrics Mechanical Spectrometer, RMS 7200) was used to measure the shear stresses and the first normal stress differences at different temperatures in the low shear rate region. An Instron Capillary viscometer was used to measure shear viscosity data in the high shear rate region. The basic rheological data for BHS, three batches of MBM, and LSB resins are tabulated in Tables 9 to 13, respectively. The data for MBM-I resin were obtained after removing the pellets of unknown polymer of density less than one. The basic rheological data for a washed MBM-II resin (to remove more extractable oligomers) are tabulated in Table 14. A plot of shear viscosities for BHS and MBM-I resin is shown in Figure 7.1. It can be noted from Tables 9 to 13 that BHS resin had higher viscosity than MBM and LSB resins at a given temperature as to be expected from molecular weight data. The shear viscosities of MBM-I and MBM-II resins are almost identical as can be seen from Tables 10 and 11. However, the shear viscosities of MBM-III resin were slightly lower than those for MBM-II resin as can be seen from Tables 12 and 13. LSB resin showed significant degradation and bubble formation when placed in the cone-and-plate gap above 245 °C. This led to significantly lower shear viscosities at temperatures above 245 °C (as can be seen from Table 13) than could be expected from the zero-shear activation energy of nylon 6 resins. The shear viscosities of unwashed and washed MBM-II resin were almost identical as can be seen from Tables 11 and 14. The important parameter in a

Table 9 : Basic Rheological data of BHS resin.

Temp.= 260 °C			Temp.= 243 °C		
γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)	γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)
1.0	992	-	0.25	1516	-
1.6	998	-	0.4	1560	-
2.5	1000	-	0.6	1534	-
4.0	1055	820	1.0	1551	-
6.3	-	1576	1.6	1584	378
15.2	780	-	2.5	1568	662
30.7	694	-	4.0	-	1355
62	627	-	6.0	1482	-
156	538	-	15.4	1300	-
313	440	-	31.0	1156	-
630	381	-	63	973	-
			160	780	-
			325	610	-

Table 10 : Basic Rheological data of MBM-I resin.

Temp.= 260 °C			Temp.= 230 °C		
γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)	γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)
1.62	222	-	0.6	527	-
2.5	210	-	1.0	543	-
4.0	216	-	1.6	525	-
6.1	217	-	2.5	533	-
10	226	173	4.0	540	158
16	226	394	6.1	544	299
24.5	224	756	10	547	709
40	221	1638	16	543	1575
60	176	-	32	409	-
155	153	-	64	374	-
319	135	-	163	237	-
661	110	-	329	190	-
1745	68.6	-	665	153.5	-
3691	44.4	-	1687	111.4	-
7880	31.0	-	3418	83.7	-

Table 11 : Basic Rheological data of MBM-II resin.

Temp.= 260 °C			Temp.= 230 °C		
γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)	γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)
2.5	223	-	1.0	520	-
4.0	236	-	1.6	531	-
6.3	225	-	2.5	522	-
10	236	158	4.0	543	158
16	233	386	6.3	525	331
25	227	724	10	543	709
		-	16	537	1528

Table 12 : Basic Rheological data of MBM-III resin.

Temp.= 260 °C			Temp.= 230 °C		
γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)	γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)
1.04	184	-	0.41	436	-
1.63	200	-	0.64	449	-
2.5	207	-	1.05	486	-
4.0	215	-	1.67	486	-
6.2	204	79	2.57	483	-
10	213	155	4.1	484	158
16	211	307	6.2	489	284
25	203	645	10.1	496	630
40	201	1376	16	501	1370

Table 13 : Basic Rheological data of LSB resin.

Temp.= 260 °C			Temp.= 230 °C		
γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)	γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)
1.0	237	-	0.4	945	-
1.6	254	-	0.63	900	-
2.5	255	-	1.0	944	-
4.0	262	110	1.6	960	-
6.3	251	204	2.5	919	189
10	265	488	4.0	940	425
		-	6.3	900	850

Table 14 : Basic Rheological data of a washed MBM-II resin.

Temp.= 260 °C			Temp.= 230 °C		
γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)	γ (1/sec)	η (Pa-s)	$\sigma_{11}-\sigma_{22}$ (Pa)
2.5	227	-	1.0	557	-
4.0	236	-	1.6	561	-
6.3	225	-	2.5	533	-
10	236	220	4.0	543	268
16	230	410	6.3	525	408
25	223	804	10	548	864
		-	16	540	1724

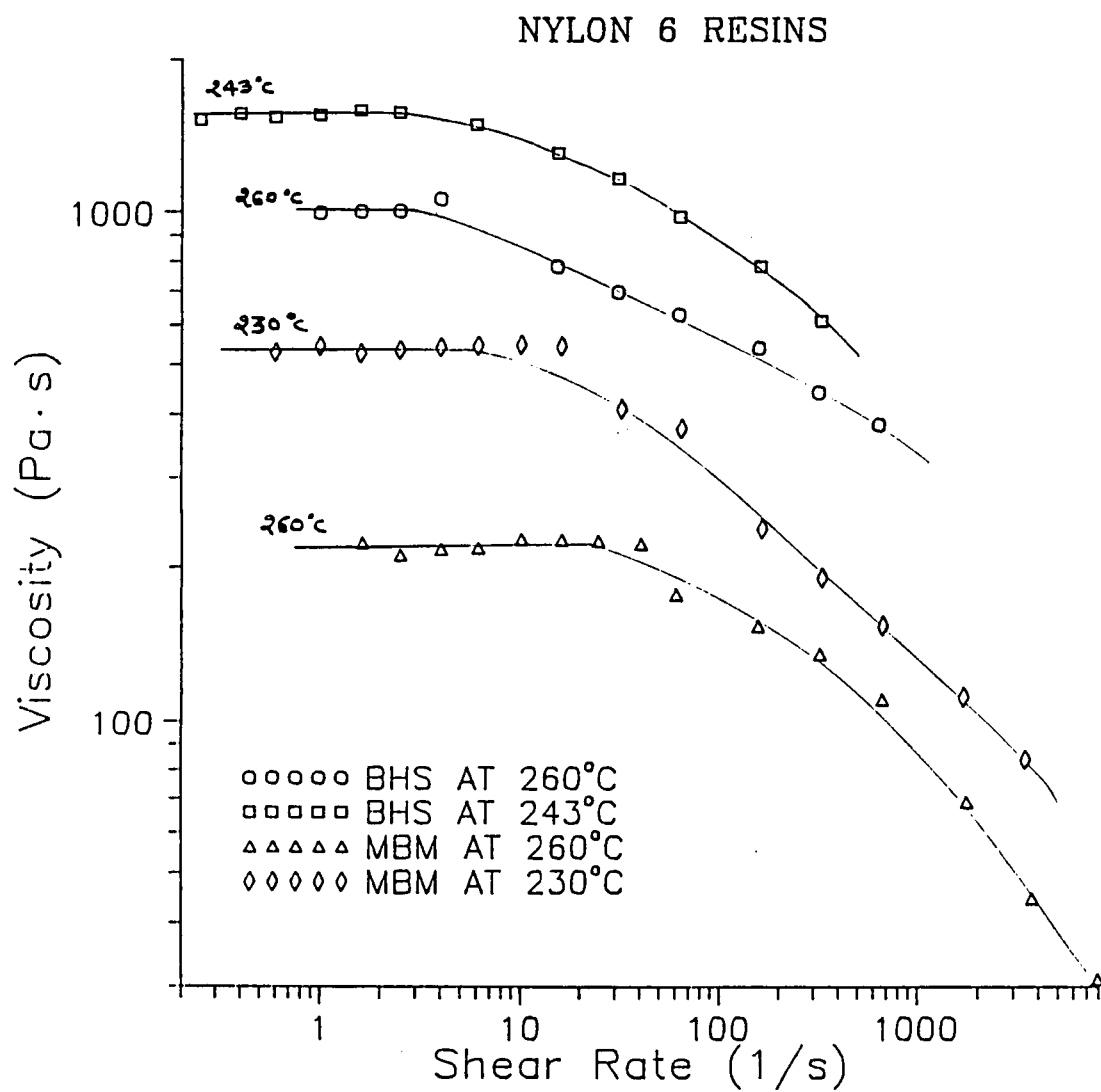


Figure 7.1. Shear viscosity data for BHS and MBM-I resins at various temperatures.

shear viscosity measurement is a zero-shear viscosity which can be obtained from the extrapolation of low shear rate data measured using a cone-and-plate rheometer at a given temperature. The zero shear viscosity at a given temperature can be correlated to weight average molecular weight and zero shear viscosity data of a given resin can be correlated with temperature using an Arrhenius type expression ($\eta_o(T) = K \exp(B/T)$, where $B=A/R$, A =energy of activation and R =Universal gas constant). The variation of zero-shear viscosity with temperature for various nylon 6 resins are as follows:

For BHS:

$$\eta_o = 2.236 \times 10^{-3} \exp \left[\frac{6948}{T + 273} \right] \quad (\text{Pa} - \text{s}) \quad [7.1.1]$$

For MBM-I and MBM-II:

$$\eta_o = 2.196 \times 10^{-4} \exp \left[\frac{7411}{T + 273} \right] \quad (\text{Pa} - \text{s}) \quad [7.1.2]$$

For MBM-III:

$$\eta_o = 2.1577 \times 10^{-4} \exp \left[\frac{7362}{T + 273} \right] \quad (\text{Pa} - \text{s}) \quad [7.1.3]$$

From the above data, it can be shown that the zero-shear activation energy of BHS and MBM resins are 13.8 and 14.7 Kcal/mol, respectively. Kemblowski and Torzecki (138) have reported the value of 13.63 Kcal/mol for the activation energy of nylon-6 for shear flow. This would give $B=6860$ °K.

7.2 Melt Spinning of Allied BHS, LSB and MBM Resins

One of the objectives of this research was to do basic rheological,

crystallization kinetics and melt spinning studies of various nylon 6 resins supplied by Allied Fibers. The basic rheological studies on Allied nylon 6 resins are described earlier in section 7.1. The quiescent isothermal and nonisothermal crystallization kinetics studies of BHS and MBM-I resin are described in chapter 6. The analysis of melt spinning data on CN 9984 and BHS resins obtained by Bheda using improved inversion procedure and spinline model is described in chapter 5. The analysis of melt spinning data on CN 9984 and BHS resins proved the validity of the spinline model to describe nylon 6 spinline behavior. The melt spinning studies of various Allied nylon 6 resins are described here. The measured spinline viscosity and the heat transfer correlation data will be used in the spinline model for simulating Allied melt spinning processes.

The details of the spinning procedure used are described earlier in the chapter 3 under experimental procedure. The summary of the experimental processing conditions used is given in Table 15. The first batch of MBM resin (MBM-I) always gave unsteady spinline and phenomenon similar to draw resonance was observed. After several attempts and changes in conditions did not lead to a steady spinline, the batch was sent back to Allied Fibers for examination. The batch was found to be contaminated with pellets of density less than one which also had air pockets inside them. Two other batches of MBM resins (MBM-II and MBM-III) were supplied by Allied Fibers. From basic rheological studies, it was determined that MBM-III had slightly lower zero-shear viscosity than MBM-II resin as described in section 7.1. The results of melt spinning studies of these MBM resins and also BHS and LSB resins will now be described.

The diameter profiles for MBM-II and MBM-III resins spun at various take-up velocities are shown in Figure 7.2. The measured diameter at a particular position on the spinline was the result of statistical analysis of 2000 data points collected using Zimmer and IBM PC/AT. In one set of experiments, both MBM-II and MBM-III resins were

Table 15. Summary of experimental processing conditions.

Extrusion temperature	- 245 °C for all nylon 6
Mass Through rate	- 3.25 g/min
Spinneret	- Circular cross section diameter = 1000 micrometer
Spinline length	- 2.30 meters
Cooling conditions	- Stationary air, temperature = 28 °C
Take-up velocities	- 2000 - 3150 m/min

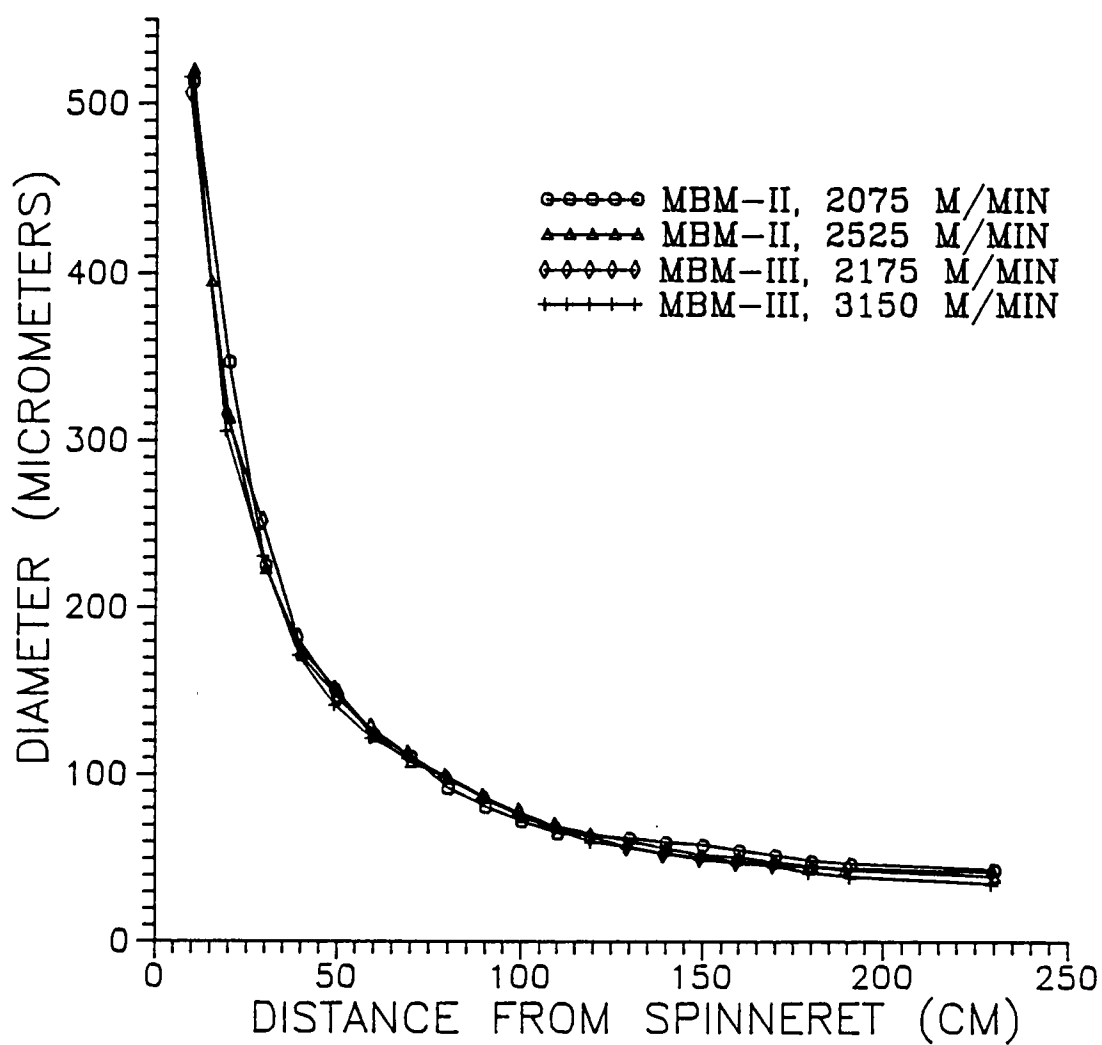


Figure 7.2. The diameter profiles for MBM-II and MBM-III resins spun at various take-up velocities.

spun under identical conditions with same compressed air pressure supplied to aspirator. The MBM-III resin exhibited slightly lower diameters in the bottom part of the spinline as measured by Zimmer and final measured diameter ($V_L = 2175$ m/min) than MBM-II resin ($V_L = 2075$ m/min). This also indicated that MBM-III resin had slightly lower spinline viscosities than MBM-II resin. In general, the take-up velocity that can be achieved at a given air pressure is lower the higher the molecular weight of nylon 6 resin. This is expected due to the higher melt viscosity of the higher molecular weight samples and consequent higher spinline stress required to achieve a particular final velocity.

The temperature profiles for MBM-II and MBM-III resins spun at same mass throughput rate of 3.25 g/min at lower take-up velocity are shown in Figure 7.3. The details of the temperature profile measurements are described earlier in Chapter 3 under experimental procedure. It has been shown by Bheda (17) that temperature profiles are relatively independent of the take-up speeds except at high speeds when crystallization can occur on the spinline. The relative independence of temperature profile with increasing take-up speed for a particular mass throughput rate seems to be the result of a competition between increased heat transfer coefficient at high speeds and the reduced residence time for a volume element to reach a given position in the spinline. However, the effect of mass throughput rate on temperature profiles is quite substantial as shown by Bheda (17). It can be seen from Figure 7.3 that the temperature profiles for both resin spun at same mass throughput rate are very similar. The temperature profiles show some scatter probably because of inherent experimental errors involved in the Infra Red thermal imaging method. The spinline tension data were measured near the bottom of the spinline with a Rothschild Tensiometer.

From the measured diameter and temperature profile, and the tension

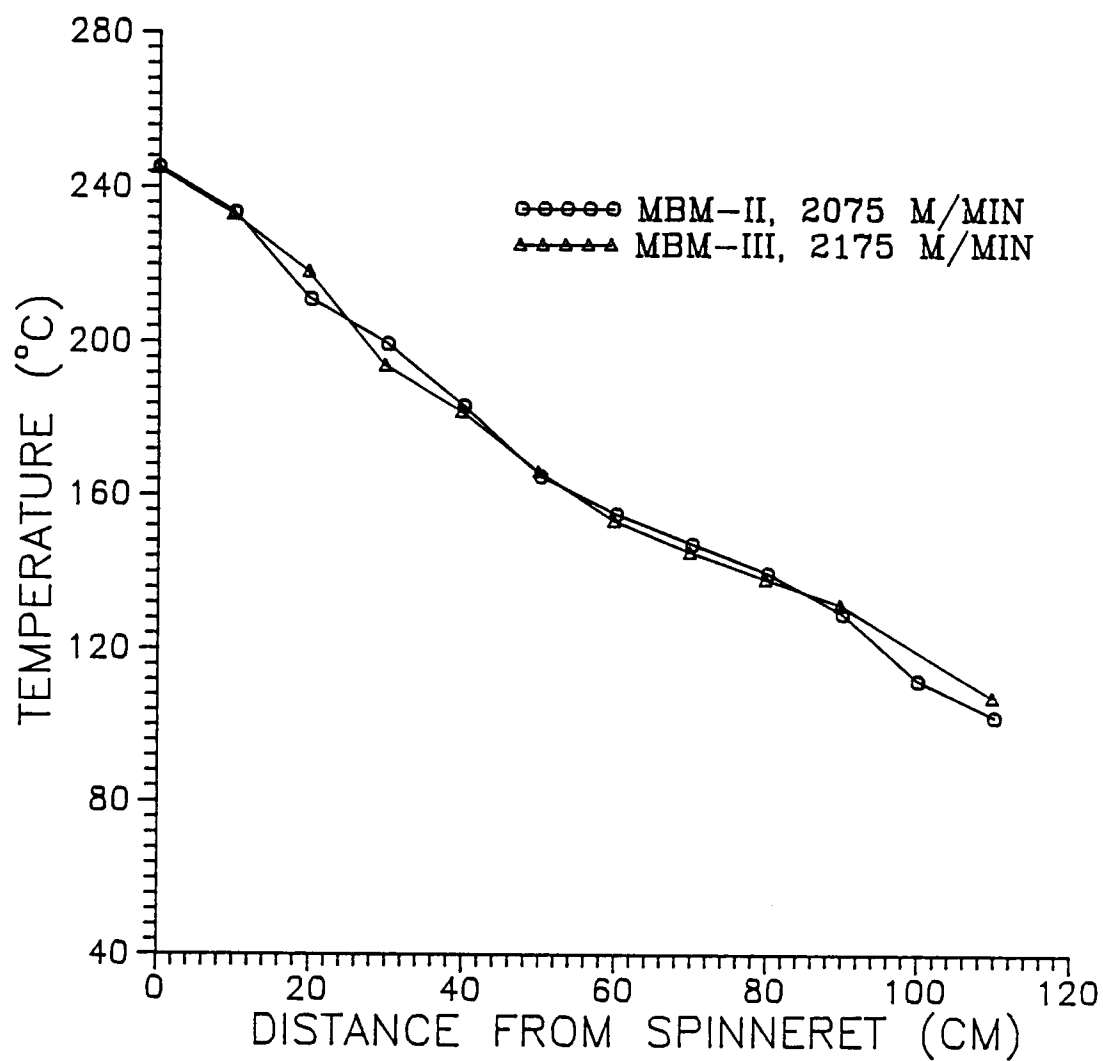


Figure 7.3. The temperature profiles for MBM-II and MBM-III resins spun at the same mass throughput rate.

measurement near the bottom of the spinline, the apparent spinline elongational viscosity and heat transfer coefficient along the spinline can be calculated using the Inversion procedure. The details of the inversion procedure is described in the section 4.3 on melt spinning studies of CN 9984 and BHS resins. The plot of computed apparent elongational spinline viscosity data as a function of reciprocal absolute temperature for both the resins at various take-up velocities is shown in Figure 7.4. Three times the zero-shear viscosity (Trouton viscosity) data measured using the cone-and-plate rheometer for both the resins are also shown in figure 7.4. It can be seen from Figure 7.4 that the spinline viscosities of MBM resins are significantly less than their Trouton viscosity. It can also be observed from the Figure 7.4 that the apparent elongational viscosity data of both the resins at lower take-up speeds are almost identical with in the experimental scatter. The inversion procedure to obtain spinline viscosities involve the calculation of elongation rates along the spinline which involves gradient of diameter profile. This leads to some scatter in the calculation of spinline viscosity data. Because of these reasons, it would not be possible to measure minor differences in spinline elongational viscosities between MBM-II and MBM-III resins which might be expected from their shear data. The minor differences in the apparent elongational viscosity data for each resin at different take-up speed may be attributed to the fact that most polymer, including nylon 6, exhibit non-Newtonian viscoelastic behavior and their viscosities depend on instantaneous deformation rate and deformation history apart from temperature. However, nylon 6 exhibit Newtonian behavior in shear over a broad shear rate range and minor differences in the apparent elongational viscosities can be disregarded in the present model calculations for Allied melt spinning processes.

The diameter profiles of BHS resin spun at two different take-up velocities and LSB resin spun at a take-up velocity of 2340 m/min are shown in the Figure 7.5. In one

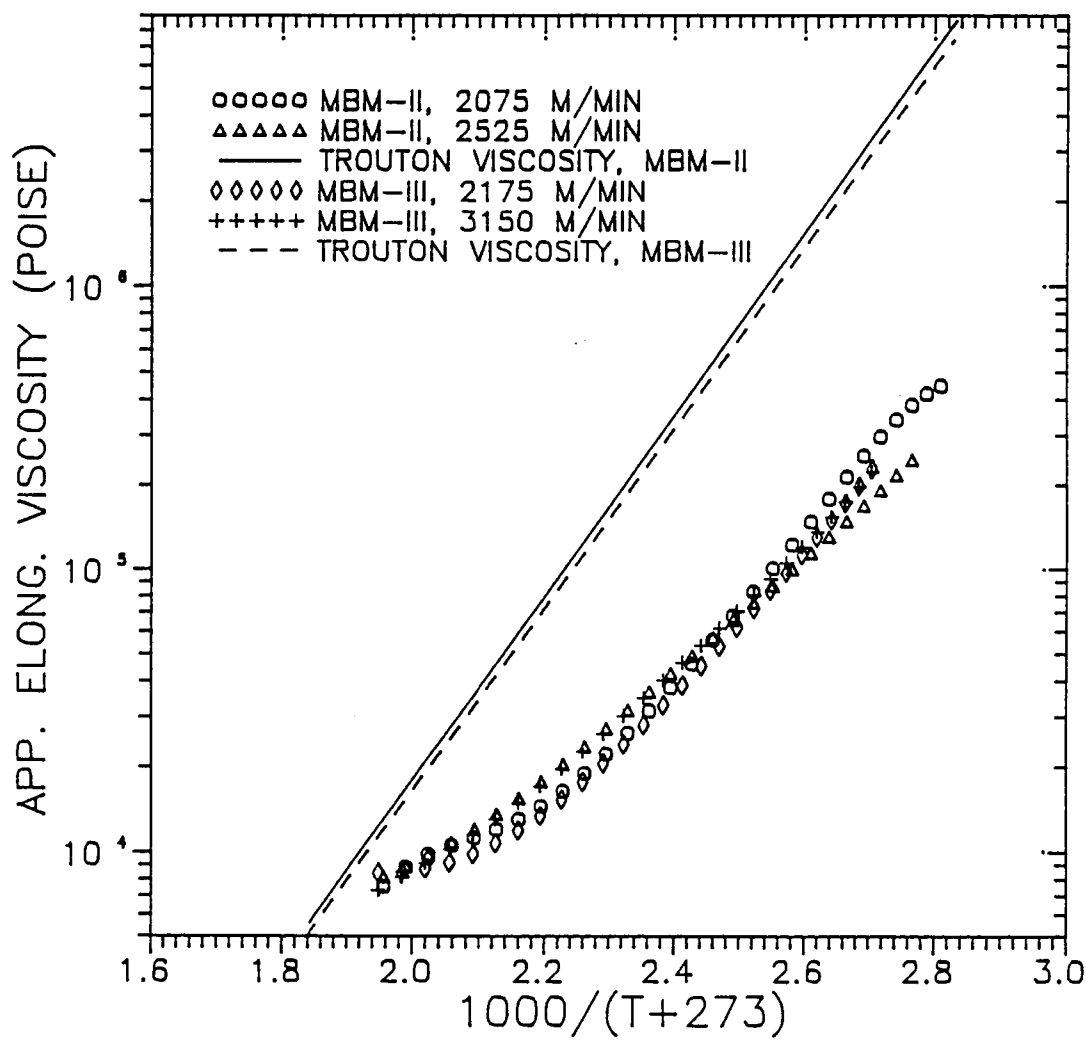


Figure 7.4. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for MBM-II and MBM-III resins.

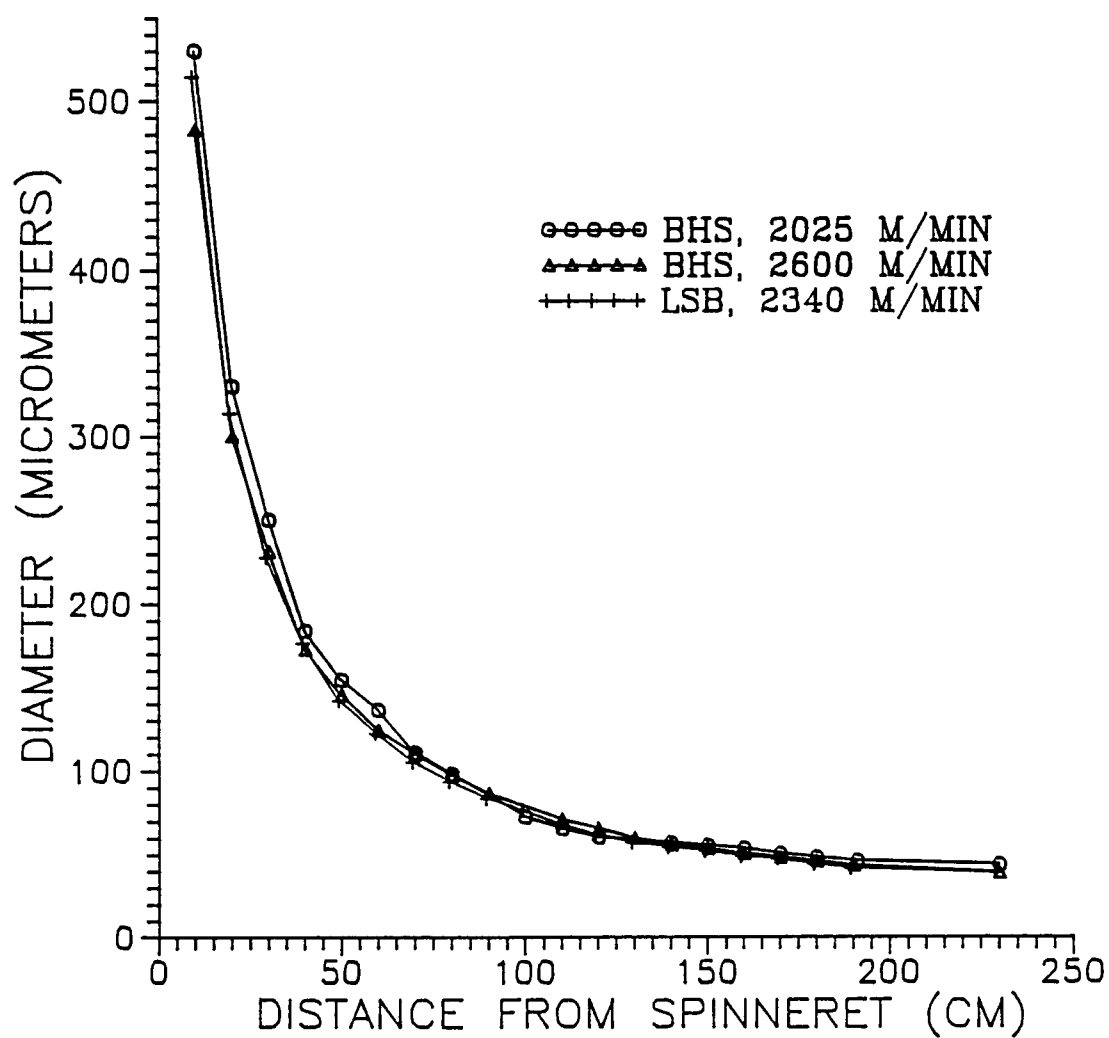


Figure 7.5. The diameter profiles of BHS and LSB resins spun at various take-up velocities.

set of experiments, both BHS and LSB resins were spun under identical compressed air pressure supplied to aspirator. The LSB resin exhibited significant lower diameters in the bottom part of the spinline as measured by Zimmer and final measured diameter ($V_L = 2340$ m/min) than BHS resin ($V_L = 2025$ m/min). The plot of computed apparent elongational spinline viscosity data as a function of reciprocal absolute temperature for both the resins at various take-up velocities is shown in Figure 7.6. Three times the zero-shear viscosity data (Trouton viscosity) measured using the cone-and-plate rheometer for BHS resin are also shown in the figure 7.6. The computed spinline viscosity data from experimental data on BHS resin at 2.993 g/min obtained by Bheda (149) are also shown in Figure 7.6 for comparison. It can be seen from Figure 7.6 that spinline viscosities of LSB resin were significantly lower than those for BHS resin. The apparent spinline elongational viscosity data for various resins are compared in Figure 7.7. It can be seen that each viscosity function follows nearly the Arrhenius temperature dependence. The resulting expression for apparent elongational viscosity in Poise are for BHS

$$\eta = 16.054 \exp \left[\frac{3815}{T + 273} \right] \quad [7.2.1]$$

and for LSB

$$\eta = 1.462 \exp \left[\frac{4415}{T + 273} \right] \quad [7.2.2]$$

and for MBM

$$\eta = 0.777 \exp \left[\frac{4585}{T + 273} \right] \quad [7.2.3]$$

Note that the apparent activation energy for spinline flow is significantly less than that obtained from the zero-shear viscosity data.

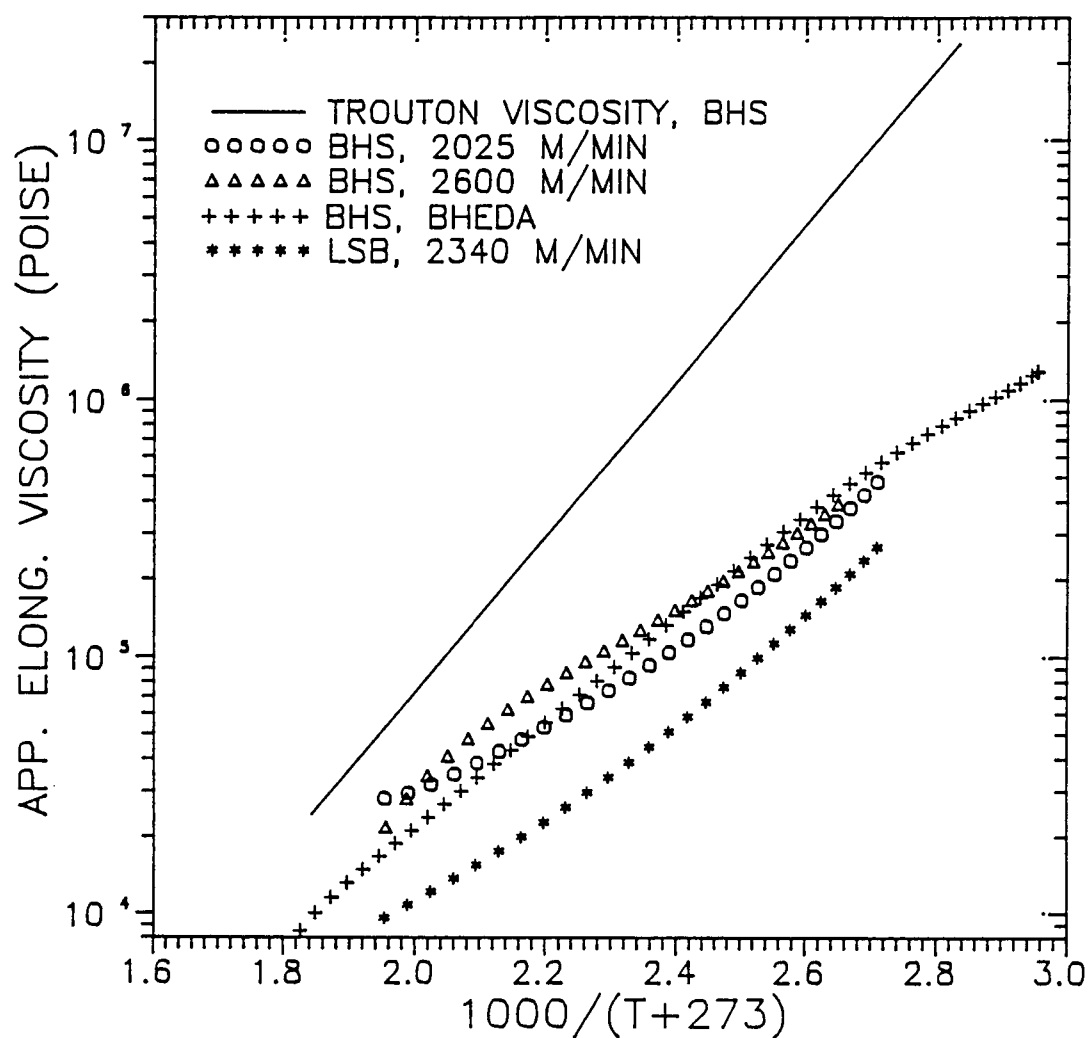


Figure 7.6. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for BHS and LSB resins.

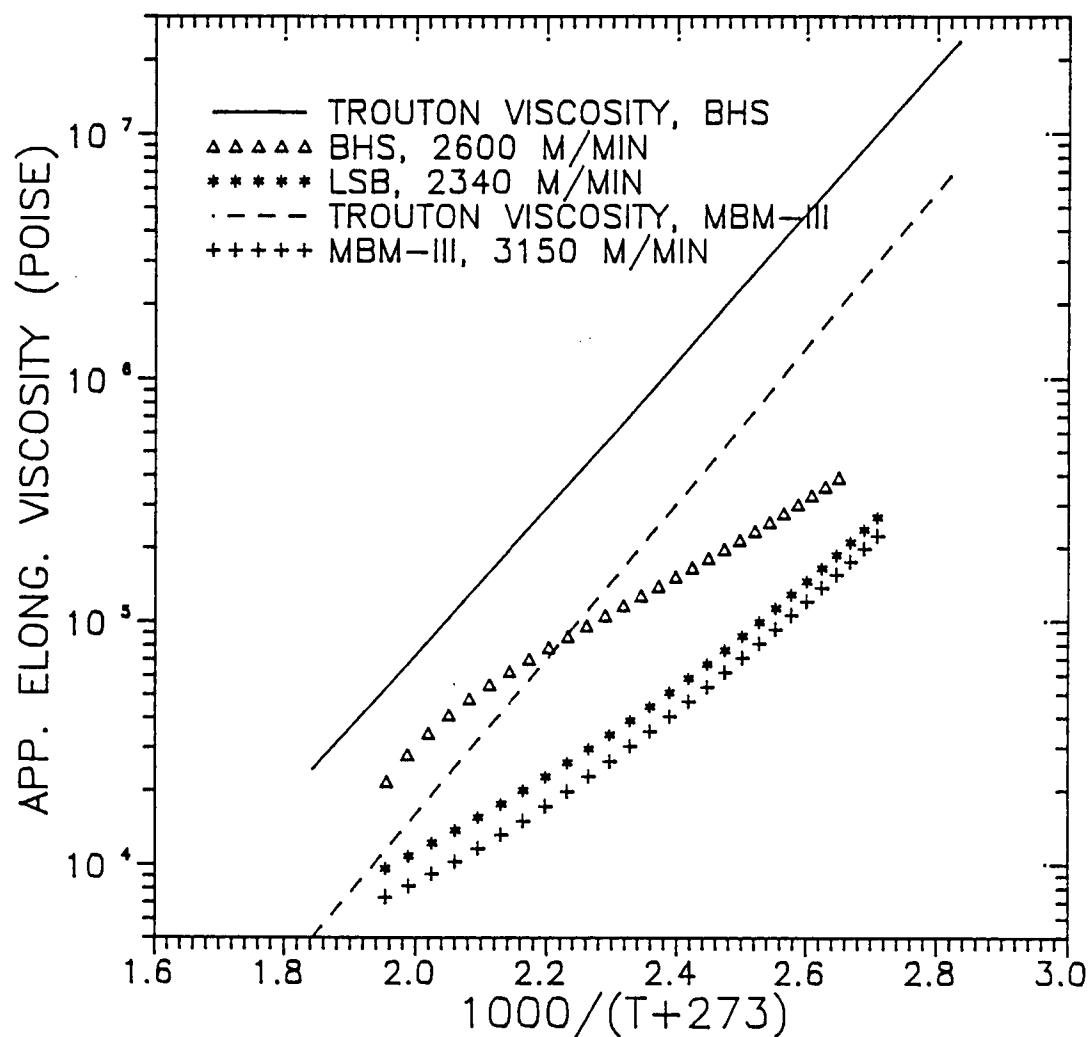


Figure 7.7. The plot of computed apparent elongational viscosity data as a function of reciprocal absolute temperature for various nylon 6 resins.

As noted earlier, the gradient of temperature profile can be used to evaluate the heat transfer coefficient along the spinline. For smoothing the temperature data, a third degree polynomial fitting of temperature versus distance data was used. The result for various resins are plotted as Figure 7.8. The Kase-Matsuo correlation (6) with and without vibrations and the results obtained from temperature profiles of BHS resin, measured by Bheda (149) using a different IR measurement technique, are also plotted. Note that the measured heat transfer coefficient includes the radiational heat transfer which may account for about 10 percent of total heat transfer in first 10 centimeters of the spinline for nylon 6. However, the radiational component in melt spinning is negligible below about 200 °C. Also the free convection may be significant in the initial part of the spinline as fiber velocities are low. However, forced convection predominates in major part of the spinline and hence, the heat transfer coefficient can be correlated with air Reynold number or alternatively, with (velocity/Area) correlation. It can be seen from the Figure 7.8 that the measured heat transfer coefficients are somewhat different than the Kase-Matsuo correlation with vibrations obtained using heated wire experiments. Also, the measured heat transfer coefficients are somewhat different than those obtained from temperature profiles measured by Bheda using a different IR measurement technique. The present on-line temperature measurement method is based on the emissivity calibration technique and is more accurate than the previous method used by Bheda (17) using an IR microscope with a black body of known temperature behind the running filament. The calculated correlation for the heat transfer coefficient in cgs units is

$$HTC = 1.47 \times 10^{-4} \left[\frac{Vel}{Area} \right]^{0.266} \quad [7.2.4]$$

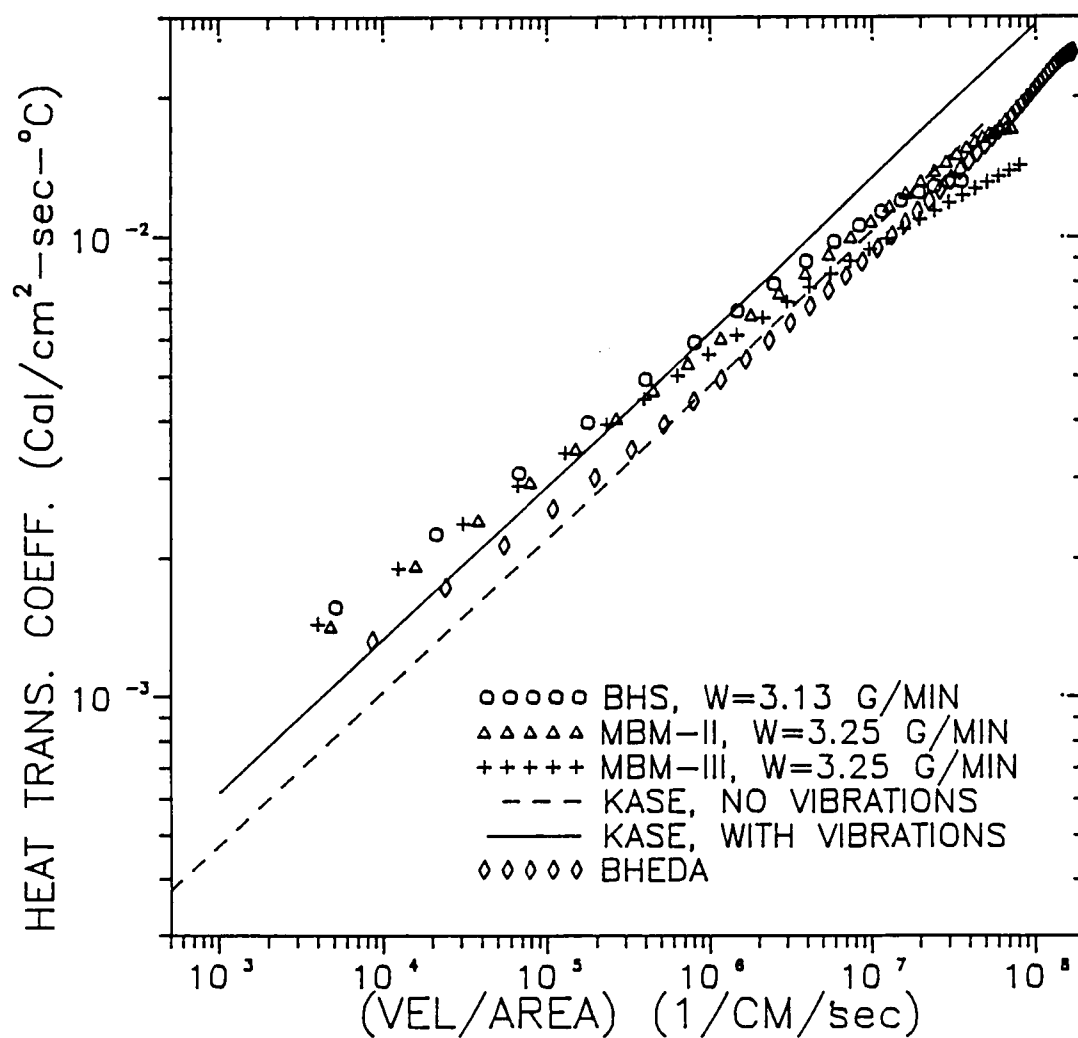


Figure 7.8. The plot of calculated heat transfer coefficient for various resins.

These results for apparent elongational viscosity function and heat transfer correlation will be used as input parameters with appropriate Allied spinning process parameters to model Allied melt spinning processes. The results of the simulations were reported separately to Allied Fibers. Various aspects of model simulations and its applications in understanding the role of various process and resin variables in determining the spinline behavior are described in the next chapter using fictitious process conditions.

CHAPTER 8

APPLICATIONS OF THE NEWTONIAN SPINLINE MODEL

Various process and resin variables that affect the spinline behavior were described earlier in chapter 4. The detailed description of the Newtonian spinline model was also given in chapter 4. Applications of the spinline model in understanding the role of various process and resin variables in determining spinline dynamics and structure development are described here. The summary of the fictitious process conditions chosen for the simulations is given in Table 16.

The spinline profiles have been simulated for these process conditions using primarily the MBM resin data for circular spinneret and triangular spinneret (of equal sides) geometry of same cross-sectional area with no shape change along the spinline. The measured apparent elongational viscosity function (Equation [7.2.3]) and its extrapolation near T_g using the WLF equation as well as the measured heat transfer correlation with a factor to account for cross-flow (Equation [7.2.4]) were used in the spinline model. The spinline profiles have also been simulated for the same process conditions using BHS resin data to show the effect of using a different molecular weight resin on the spinline behavior.

The diameter, temperature, stress and amorphous birefringence profiles for circular filament spun at 2000 m/min at two throughput rates are shown in Figures 8.1 to 8.4, respectively. The amorphous and total birefringence profiles for the same conditions are compared in Figure 8.5. The effect of throughput rate on the spinline temperature can be seen from Figure 8.2. At lower throughput rate, the cooling is more rapid (due to

Table 16. Summary of process conditions chosen for the simulation.

Extrusion temperature	- 250 °C
Mass Through rate	- 5.0 g/min
Spinneret	- Circular cross section diameter = 700 micrometer
Sinline length	- 4.0 meters
Cooling conditions	- Quench Zone; 0.1 to 1 meter. Cross-flow air, temperature = 20 °C Cross-flow air, velocity = 40 cm/sec Beyond quench zone, temp. = 35 °C
Take-up velocities	- 2000 - 7500 m/min

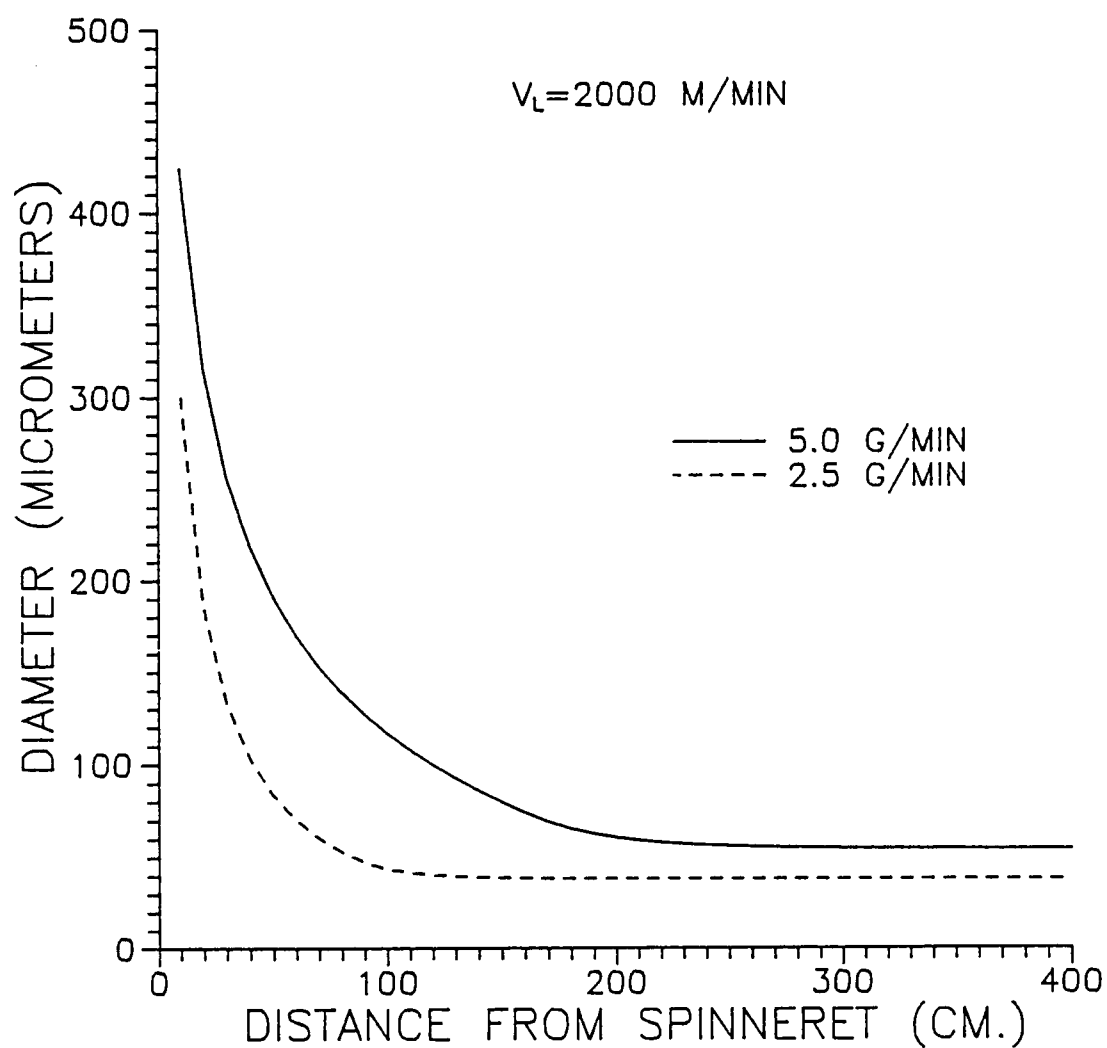


Figure 8.1. The predicted diameter profiles for circular filament spun at 2000 m/min at two throughput rates.

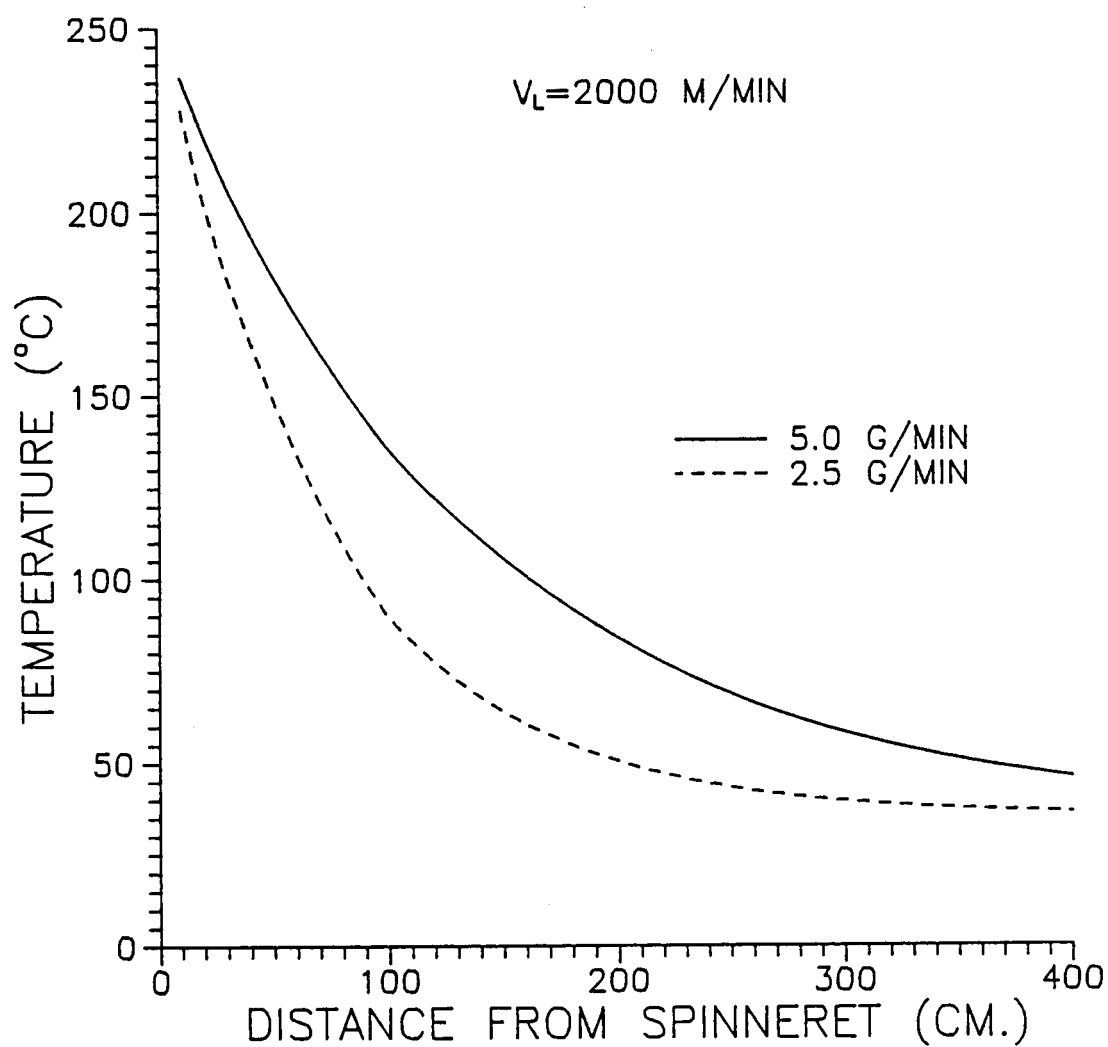


Figure 8.2. The predicted temperature profiles for circular filament spun at 2000 m/min at two throughput rates.

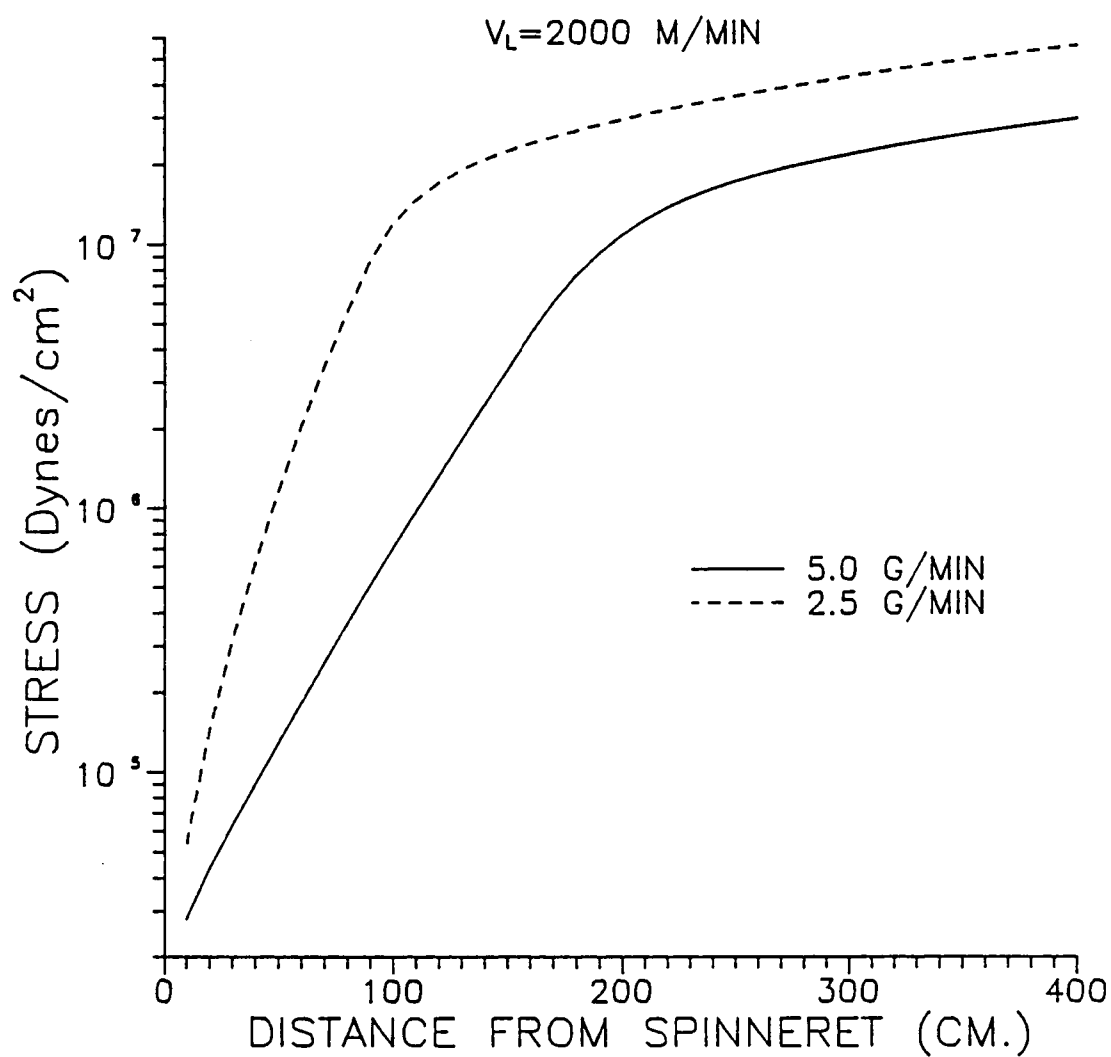


Figure 8.3. The predicted stress profiles for circular filament spun at 2000 m/min at two throughput rates.

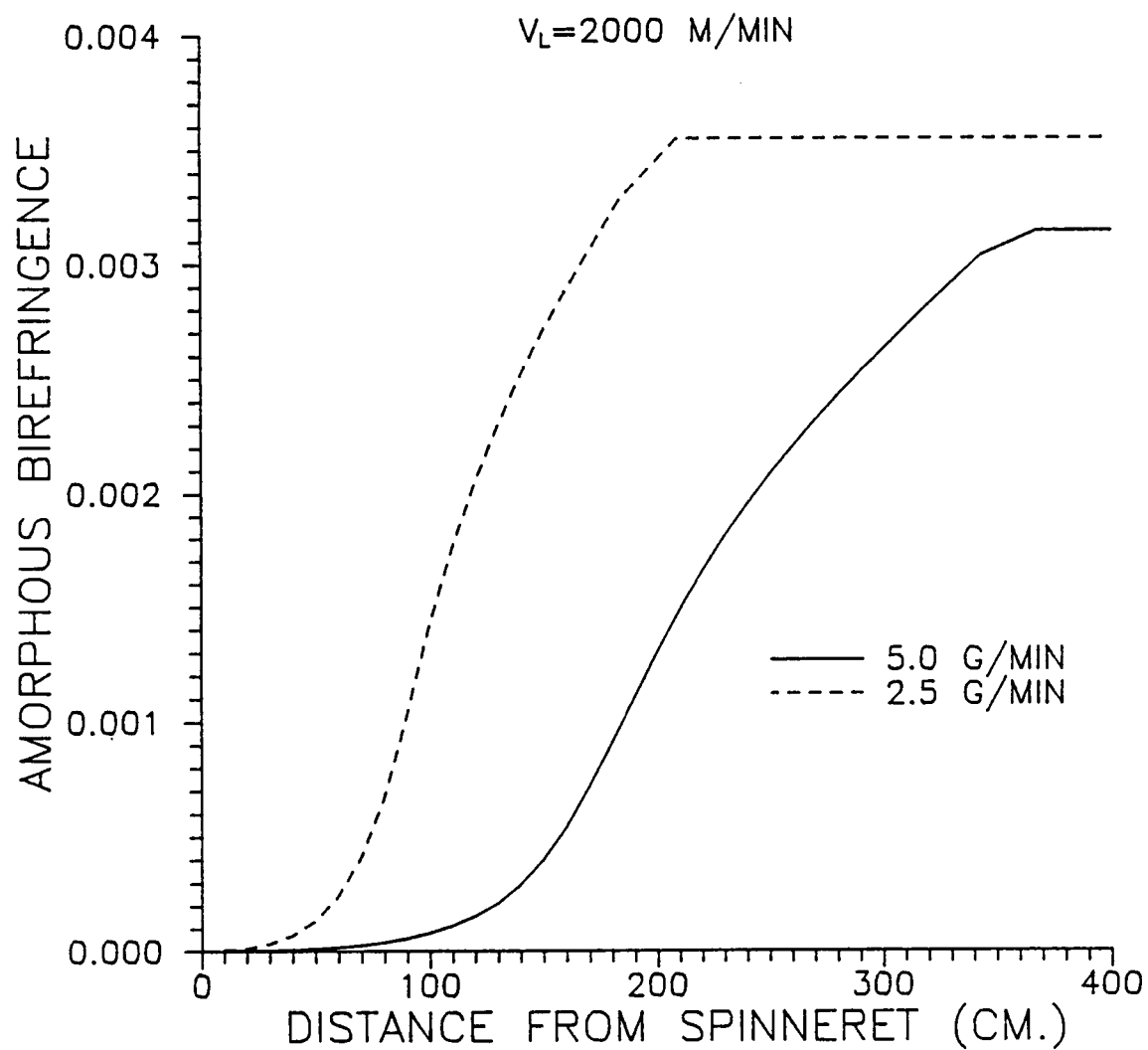


Figure 8.4. The predicted amorphous birefringence profiles for circular filament spun at 2000 m/min at two throughput rates.

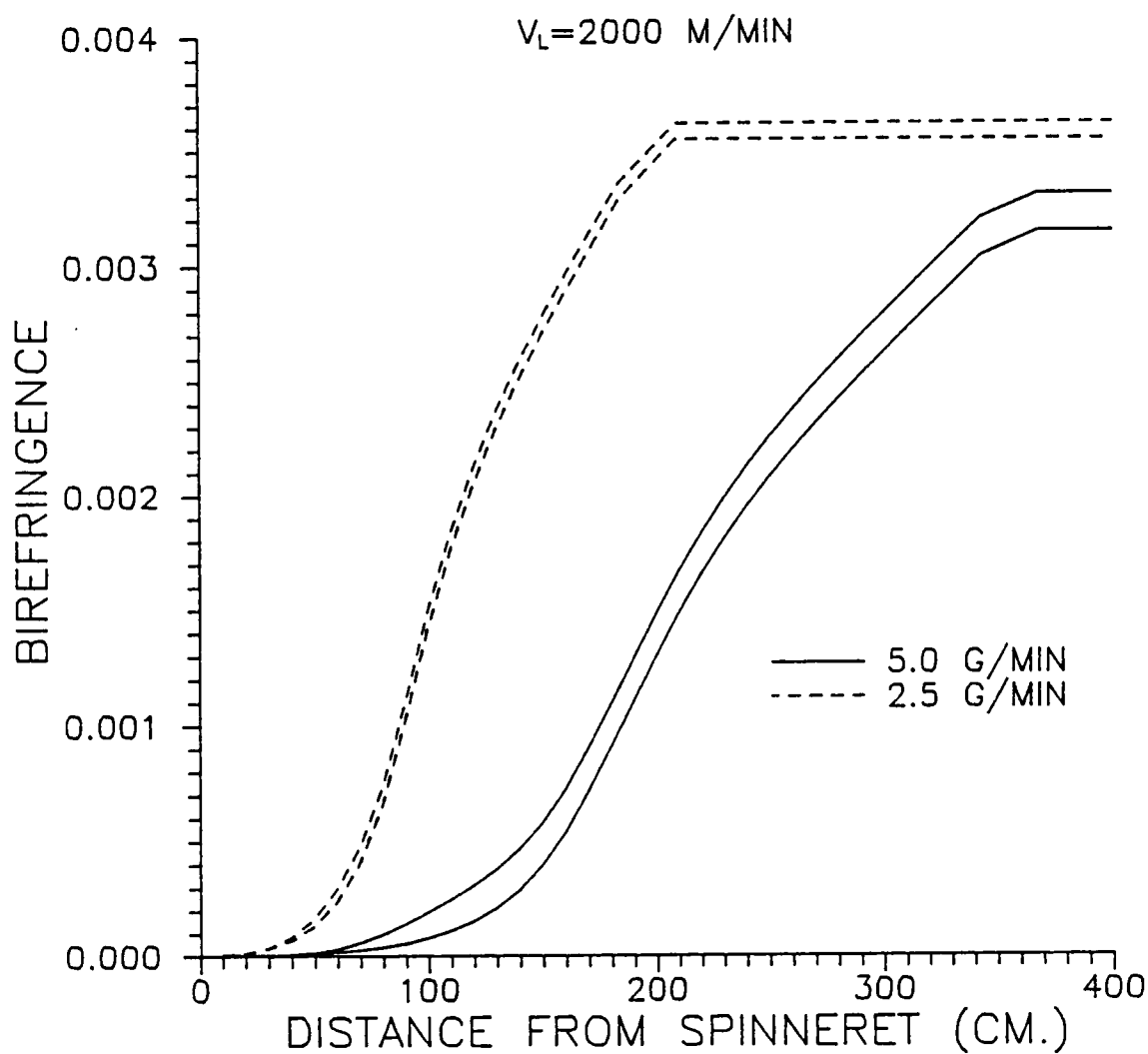


Figure 8.5. The predicted amorphous and total birefringence profiles for circular filament spun at 2000 m/min at two throughput rates.

lower spinline mass) and lower temperatures are obtained at any given spinline distance than at the higher throughput rate as can be seen from Figure 8.2. This also leads to more draw down in the upper part of the spinline for lower throughput rate as compared to higher throughput rate as can be seen from Figure 8.1 for diameter profiles. It can be seen from Figure 8.3 that higher spinline stresses are obtained at the lower throughput rate as compared to higher throughput rate for the same take-up velocity. This is partially because lower spinline temperatures are obtained at lower throughput rate requiring higher stresses to achieve similar deformation. Note that the draw ratio and final diameter (denier) are different for the two cases even though the final velocity is the same. The higher draw ratios obtained for lower throughput rate would also lead to higher stresses. According to the stress-optical law, the amorphous birefringence is directly proportional to the stress. Hence, higher values of amorphous birefringence (and more orientation of amorphous segments) are obtained along the spinline when higher spinline stresses are obtained for the lower throughput rate. This can be observed in Figure 8.4. For nylon 6, the amorphous birefringence contributes almost solely to the total birefringence at take-up speeds below 5000 m/min because no significant crystallization occurs on the spinline. This can be observed from Figure 8.5. Note that experimentally one can measure only total birefringence (which is the sum of amorphous and crystalline birefringence) directly. In the calculation of crystalline birefringence contribution, the crystalline orientation factor $f_c = 0.2$ was assumed, which might be appropriate at lower speeds. The crystalline orientation factor can not be predicted apriori from the model for melt spinning. It is possible to incorporate an empirical relation between the spinline stress at the freeze point and the final as-spun crystalline orientation, but this requires considerable data for evaluation of this relationship. Further, for nylon 6, there is little crystallization until rather high spinline stresses are reached. In this latter case the final crystalline orientation

is quite high ($f_c=0.8-0.9$). In this case it is satisfactory to give an estimate of the final crystalline orientation. The stress at freeze point (which determines birefringence) in the spinline (when $T=T_g$) is an important variable which decides the morphology of the spun filament and hence, the subsequent drawing of the spun filament. Note that the model did not predict significant crystallinity development (less than 2 percent) at the take-up speed of 2000 m/min as expected in case of nylon 6.

Nylon 6 is a slowly crystallizing polymer and hence, experience has shown that it does not crystallize on the spinline at take-up speeds substantially less than 5000 m/min. Industrial melt spinning of nylon 6 is usually done at such low take-up speeds that no crystallinity is developed on spinline. However, there is a recent trend in the industry towards higher take-up speeds to increase productivity. At such higher take-up speeds, enough amorphous orientation can be developed to obtain stress-induced crystallization on the spinline. The spinline model includes crystallization during melt spinning and hence can be used to predict spinline dynamics and structure development at higher take-up speeds. The empirical equations for describing stress-induced crystallization are based on an average value of amorphous orientation in the melt. Thus, they neglect the orientation distribution of amorphous segments and the effects of "selective" orientation-dependent crystallization on the orientation distribution of remaining amorphous segments. Because of the above limitations of the empirical equations describing stress-induced crystallization, crystallization rates are overpredicted in the later stages of crystallization. This was manifested in the prediction of a substantially higher temperature rise by the model than experimentally observed at high spinning speeds (149). Therefore, in the following calculations, the crystallization rate was not allowed to exceed $10,000 \text{ sec}^{-1}$. This is equivalent to assuming that the crystallization rate saturates at this value.

In order to demonstrate the use of the model for high speed spinning, the model predictions were obtained for circular filament at take-up velocities of 4000 m/min, 6000 m/min, and 7500 m/min for the throughput rate of 5 g/min. The predictions of diameter, temperature, amorphous birefringence, total birefringence and crystallinity profiles are compared for these three different take-up velocities in Figures 8.6 to 8.10, respectively. It can be seen from the Figure 8.10 that at take-up speeds of 6000 m/min and 7500 m/min, stress-induced crystallization was triggered on the spinline. This is because high spinline stresses obtained at such high speeds leads to high amorphous orientation thereby significantly increasing rate of crystallization. However, no significant crystallinity developed on the spinline at the take-up speed of 4000 m/min as can be seen from Figure 8.10. The heat released due to crystallization at higher take-up speeds leads to rise in spinline temperature as can be seen from Figure 8.7. Note that temperature profiles for all take-up speeds are identical up to the point where crystallization is triggered at higher speeds. The stress-induced crystallization leads to the solidification of the spinline at temperatures well above the glass transition temperature (T_g) as can be seen from Figures 8.6 and 8.7 for the diameter and temperature profiles, respectively. At the take-up velocity of 4000 m/min, no appreciable crystallization was obtained on spinline and solidification was obtained as spinline temperature approached T_g . It can be seen from Figure 8.8 that higher amorphous birefringence are obtained at higher take-up speeds as expected. After solidification, amorphous birefringence would remain constant as shown in Figure 8.8. At higher take-up speeds, stress-induced crystallization leads to formation of highly oriented crystallites in the filament, as noted above. Bheda (17) has reported the crystalline orientation factor as a function of take-up velocity for preconditioned nylon 6 filaments maintained at a constant temperature of 70 °F and a relative humidity of 65%. At low take-up velocities the value of the crystalline orientation

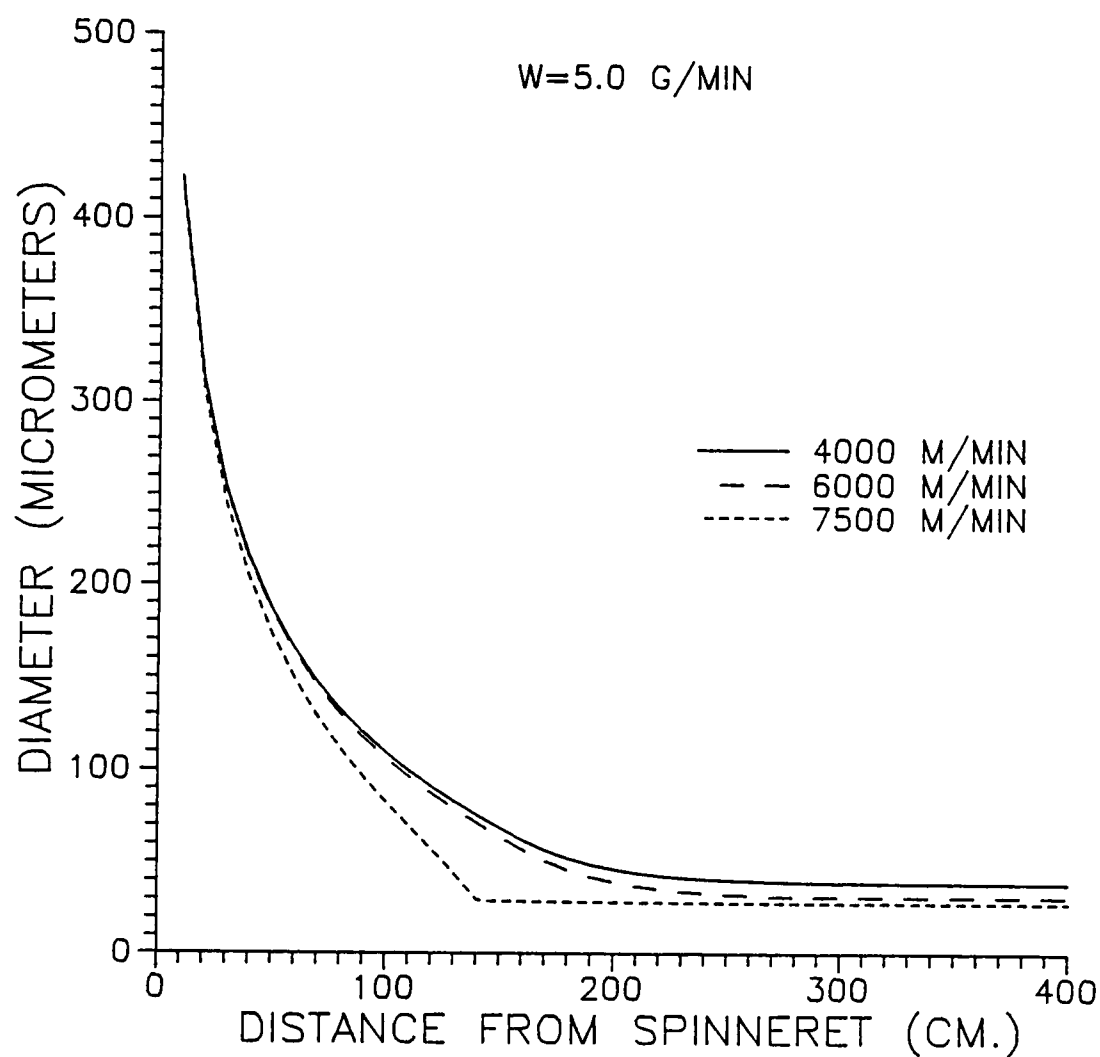


Figure 8.6. The predicted diameter profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.

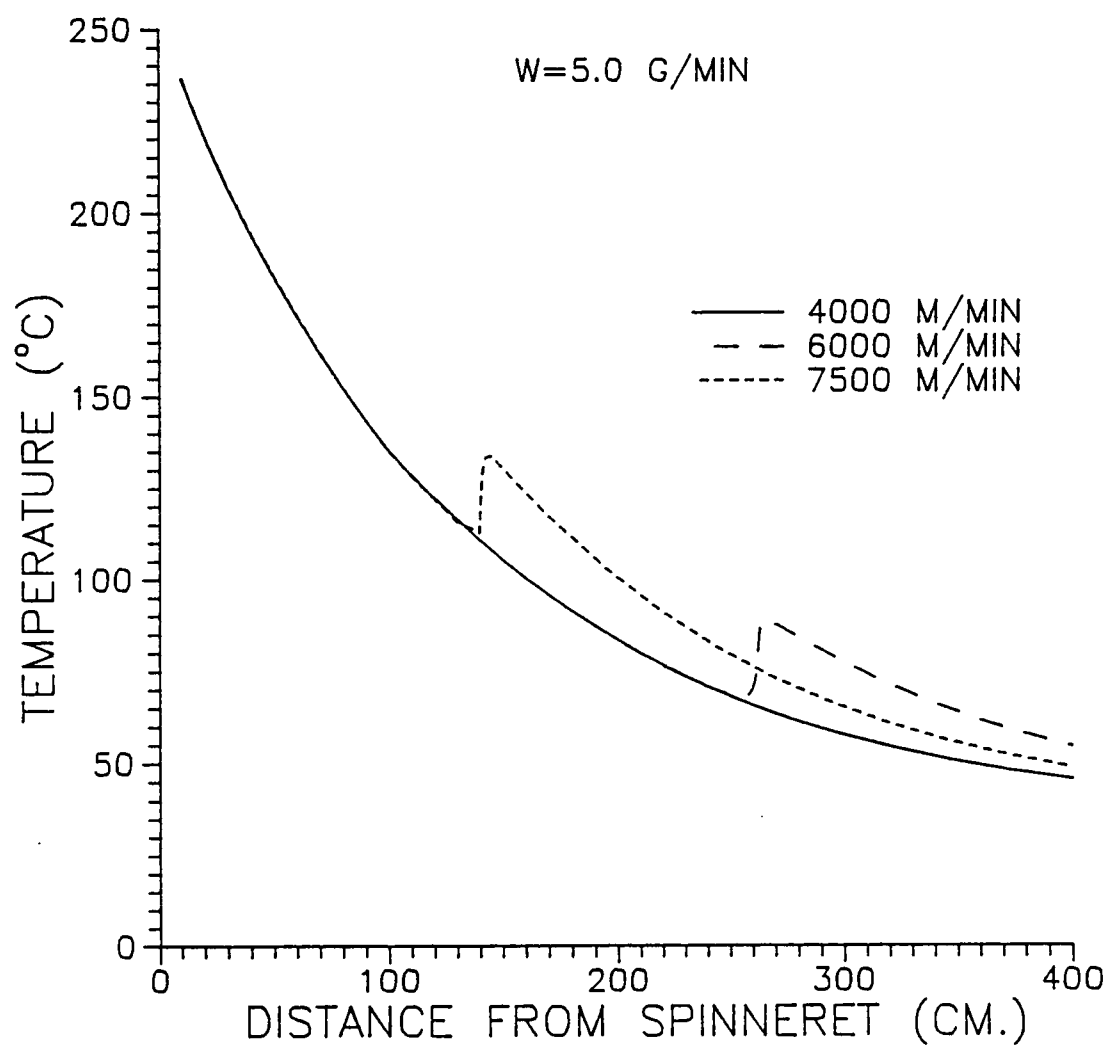


Figure 8.7. The predicted temperature profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.

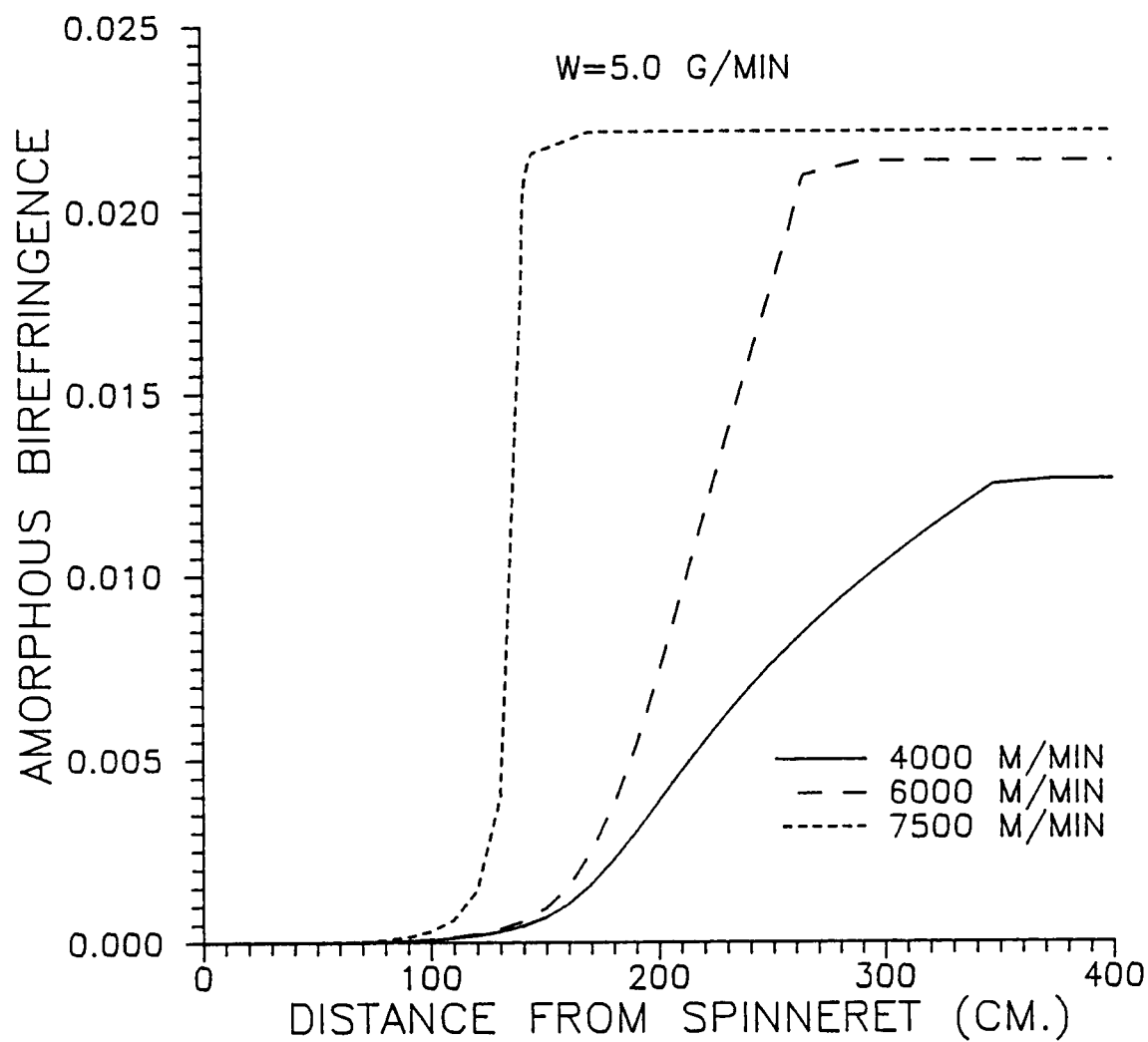


Figure 8.8. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.

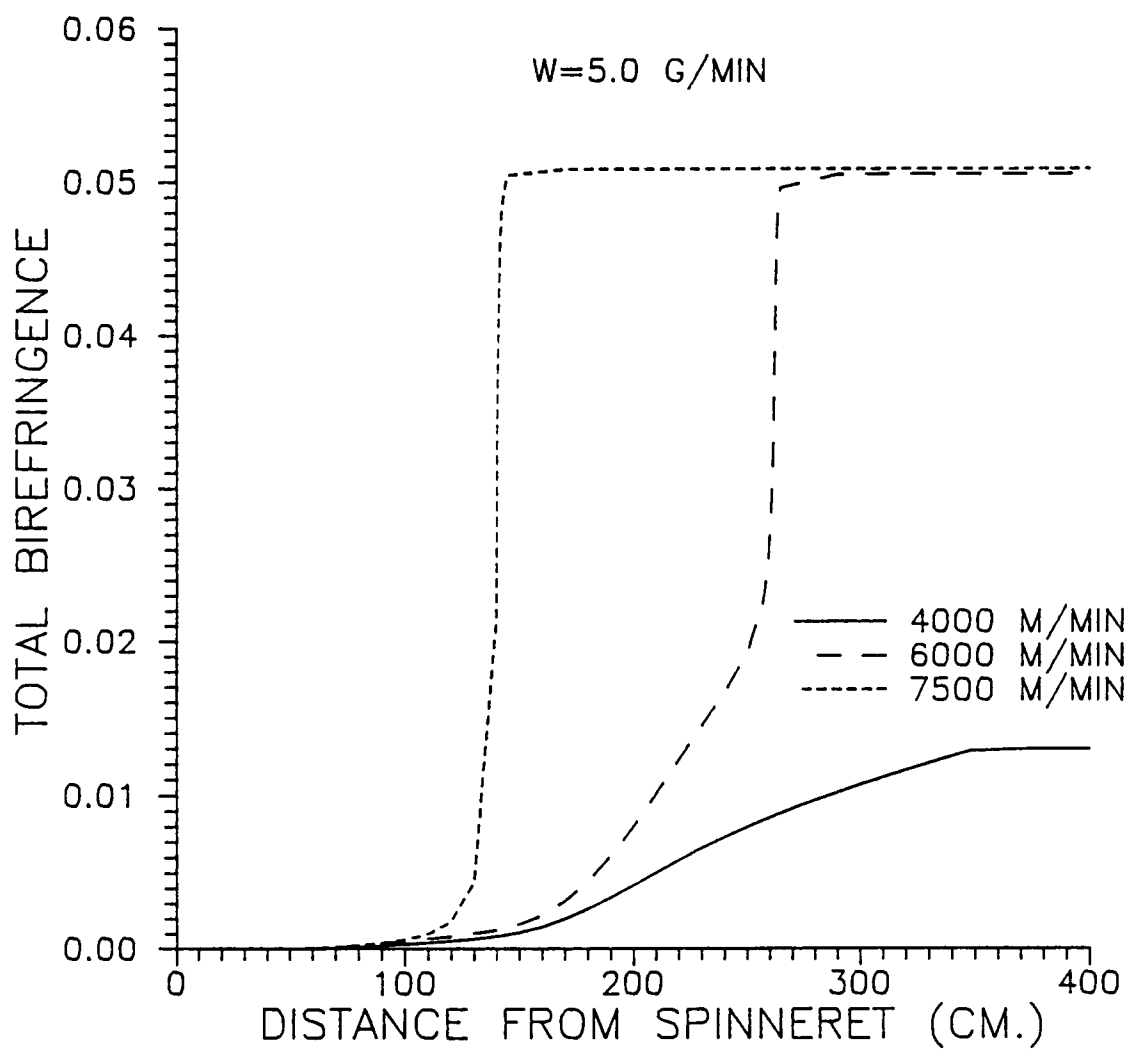


Figure 8.9. The predicted total birefringence profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.

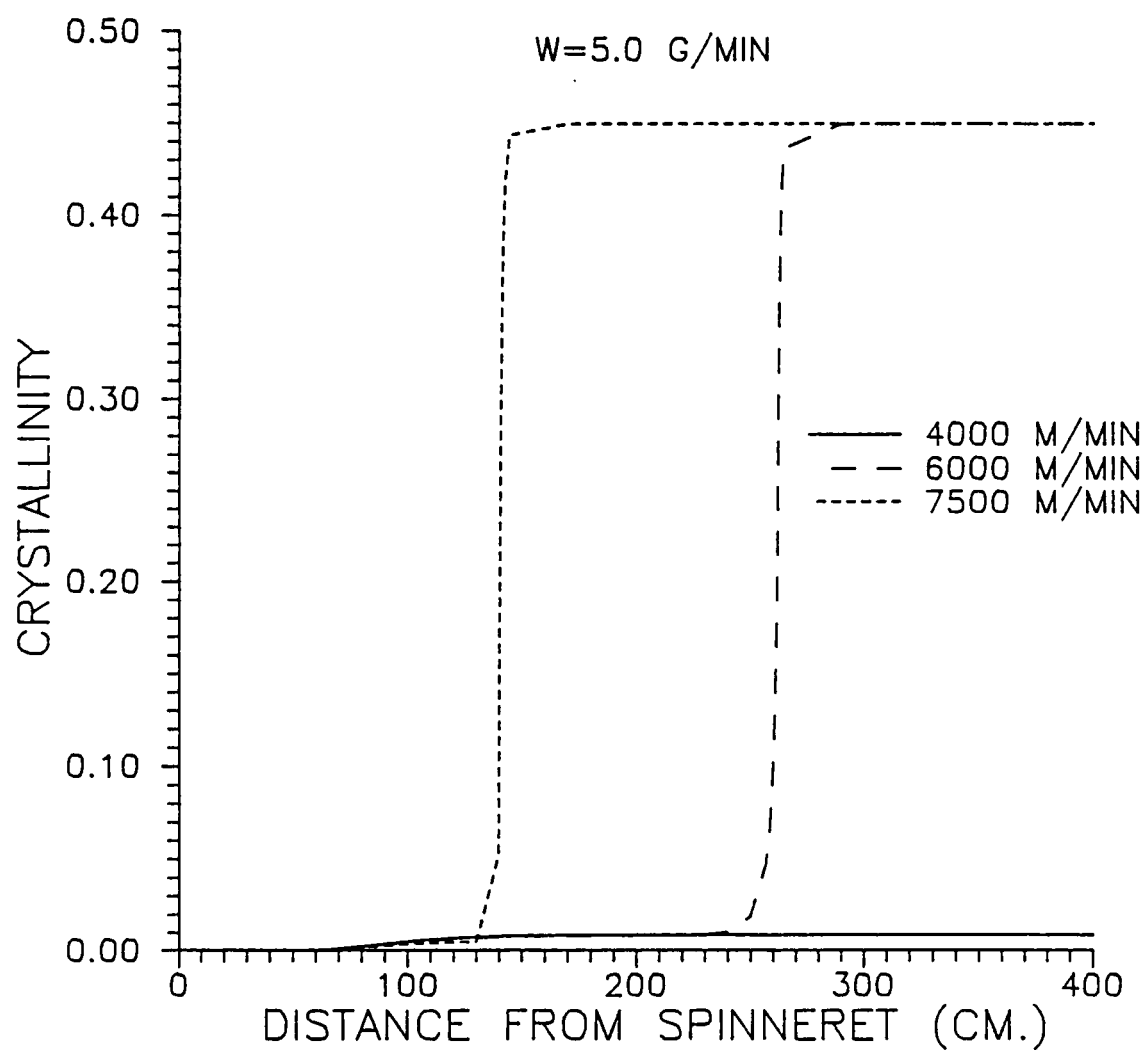


Figure 8.10. The predicted crystallinity profiles for circular filament at throughput rate of 5 g/min at three different take-up velocities.

factor was quite low (about 0.2), followed by rapid increase and then leveling off at quite high value (about 0.9) at high take-up velocities. Hence, a crystalline orientation factor of 0.9 was assumed for the calculation of total birefringence. It can be seen from Figure 8.9 for the total birefringence that at higher speeds, highly birefringent filaments are obtained due to online crystallization. The effects of resin molecular weight and mass throughput rate on spinline crystallization have been discussed in detail in chapter 5.

In order to determine the role of spinline length in controlling dynamics and structure development, spinline lengths of two and eight meters were used in the model keeping all other process conditions the same. The diameter, temperature, stress and amorphous birefringence profiles at 2000 m/min for spinline length of two and eight meters are compared with those for spinline length of 4 meters in Figures 8.11 to 8.14, respectively. Lower final filament temperatures are obtained for longer spinline as it can be seen from the Figure 8.12 for temperature profiles. For the spinline length of 2 meters, the final filament temperature predicted was 83 °C. Hence, such shorter spinline would introduce the problem of filaments sticking to each other in case of multi-filament spinning. However, for the spinline length of 4 meters, the final spinline temperature is already very close to the glass transition temperature (T_g) of nylon 6. Note that T_g of nylon 6 is 40 °C. Hence, The diameter profiles for spinline length of 4 meters and 8 meters are identical as can be seen from Figure 8.11. No further structure development would occur beyond the spinline length of 4 meters as can be seen from Figure 8.14 for amorphous birefringence. Amorphous birefringence developed in the filaments prepared from spinline length of 4 meters and 8 meters are identical and is higher compared to filaments prepared from spinline length of 2 meters. However, for longer spinline length of 8 meters, the stresses on the filament are higher as compare to for spinline length of 4 meters. Thus, no advantage is achieved for increasing the spinline length from 4 meters

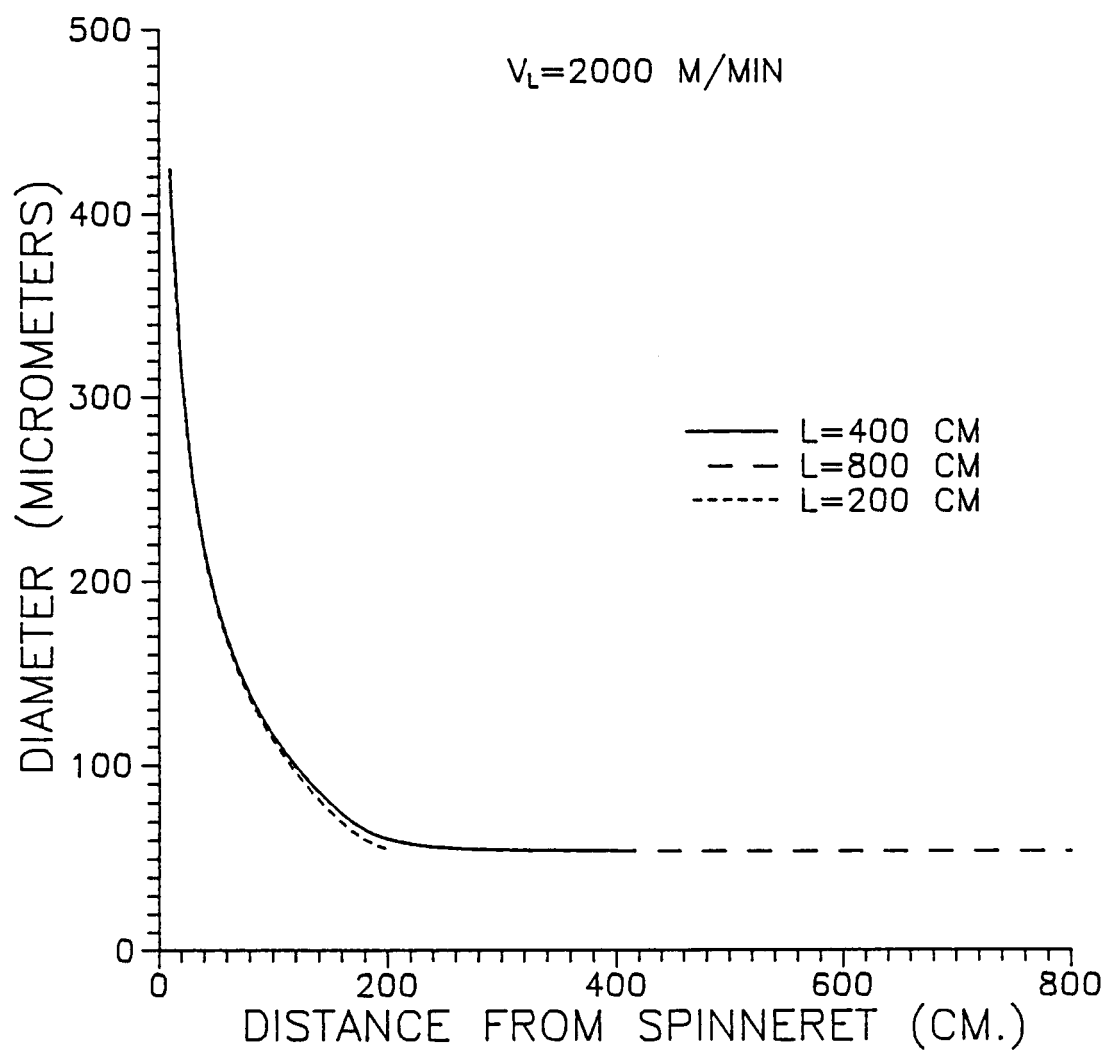


Figure 8.11. The predicted diameter profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.

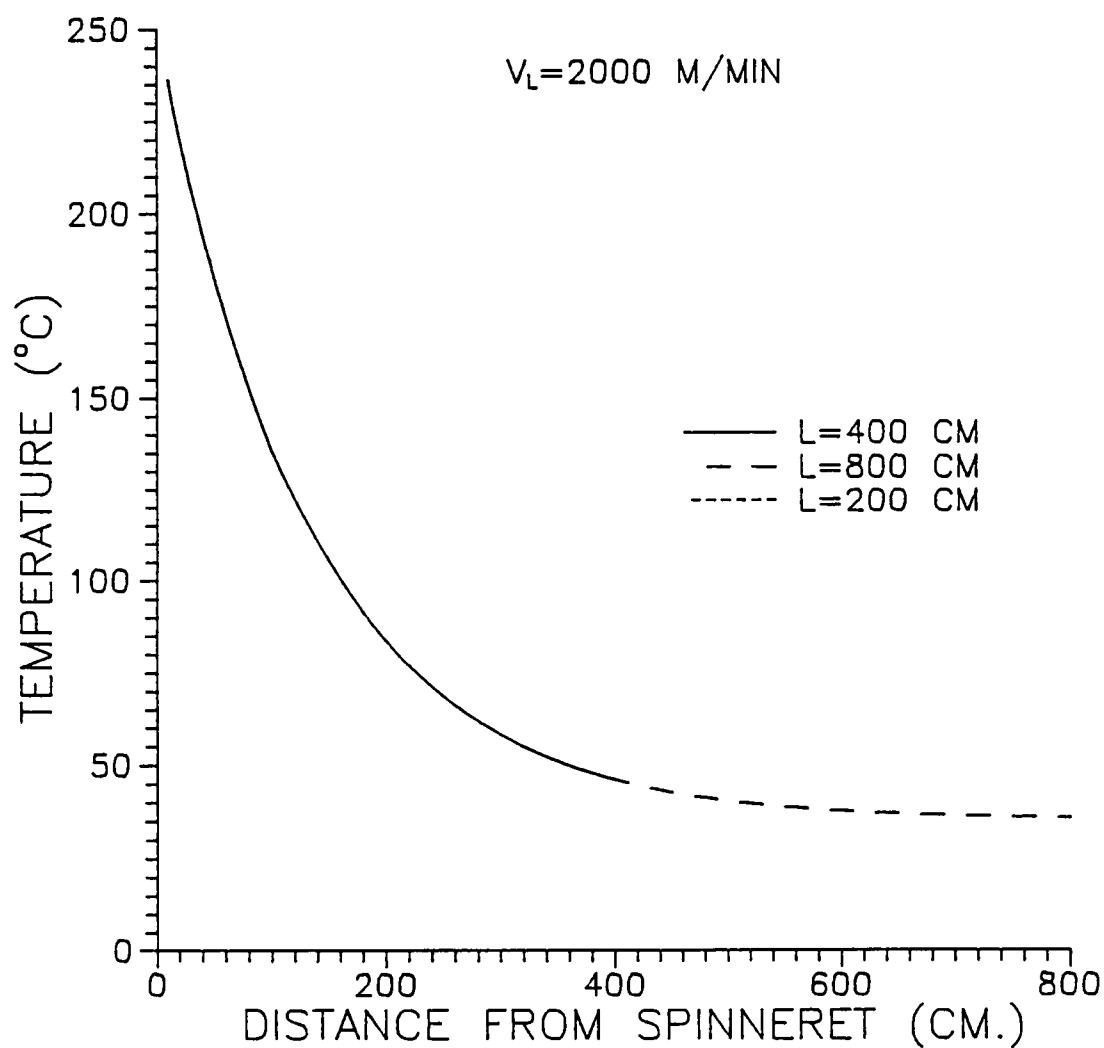


Figure 8.12. The predicted temperature profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.

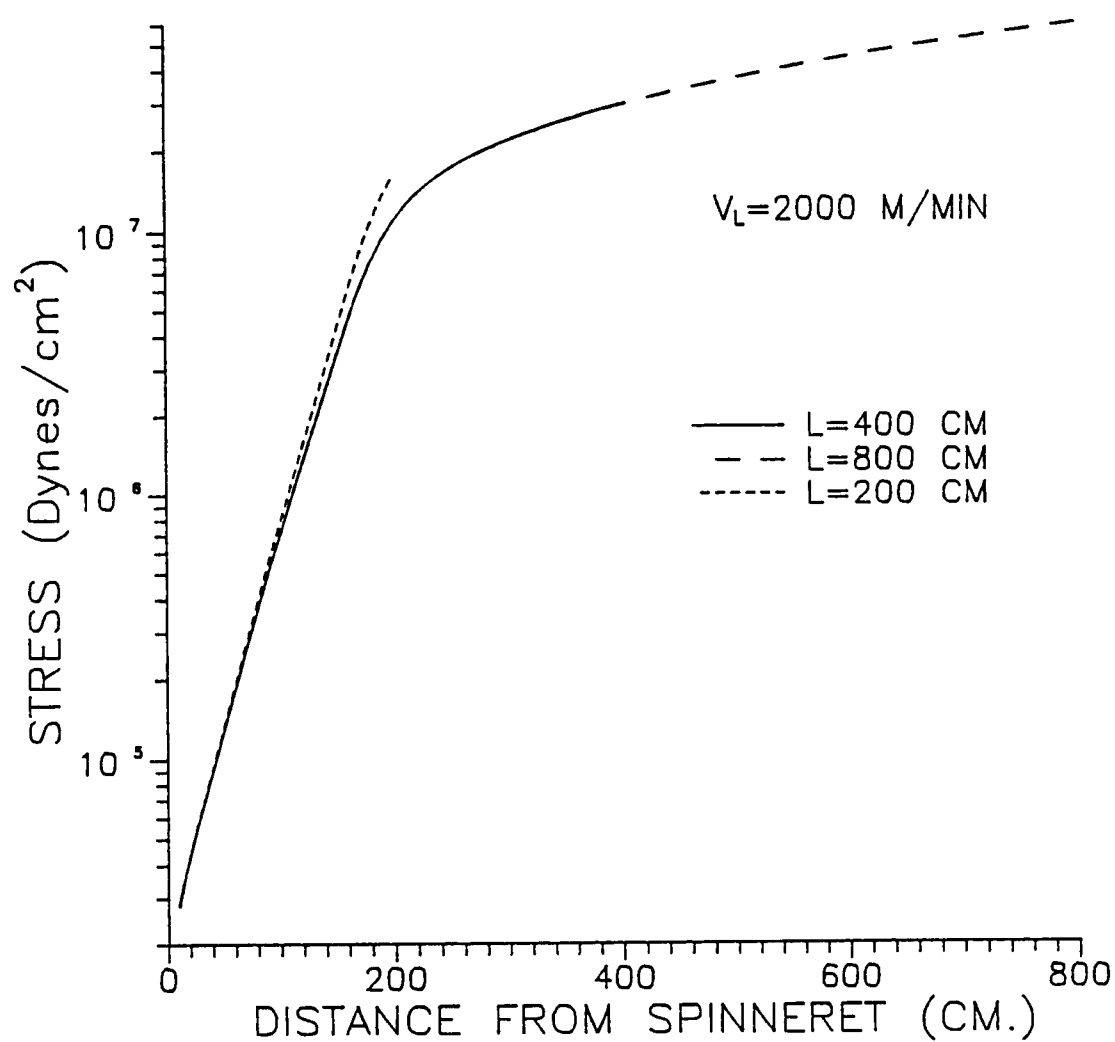


Figure 8.13. The predicted stress profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.

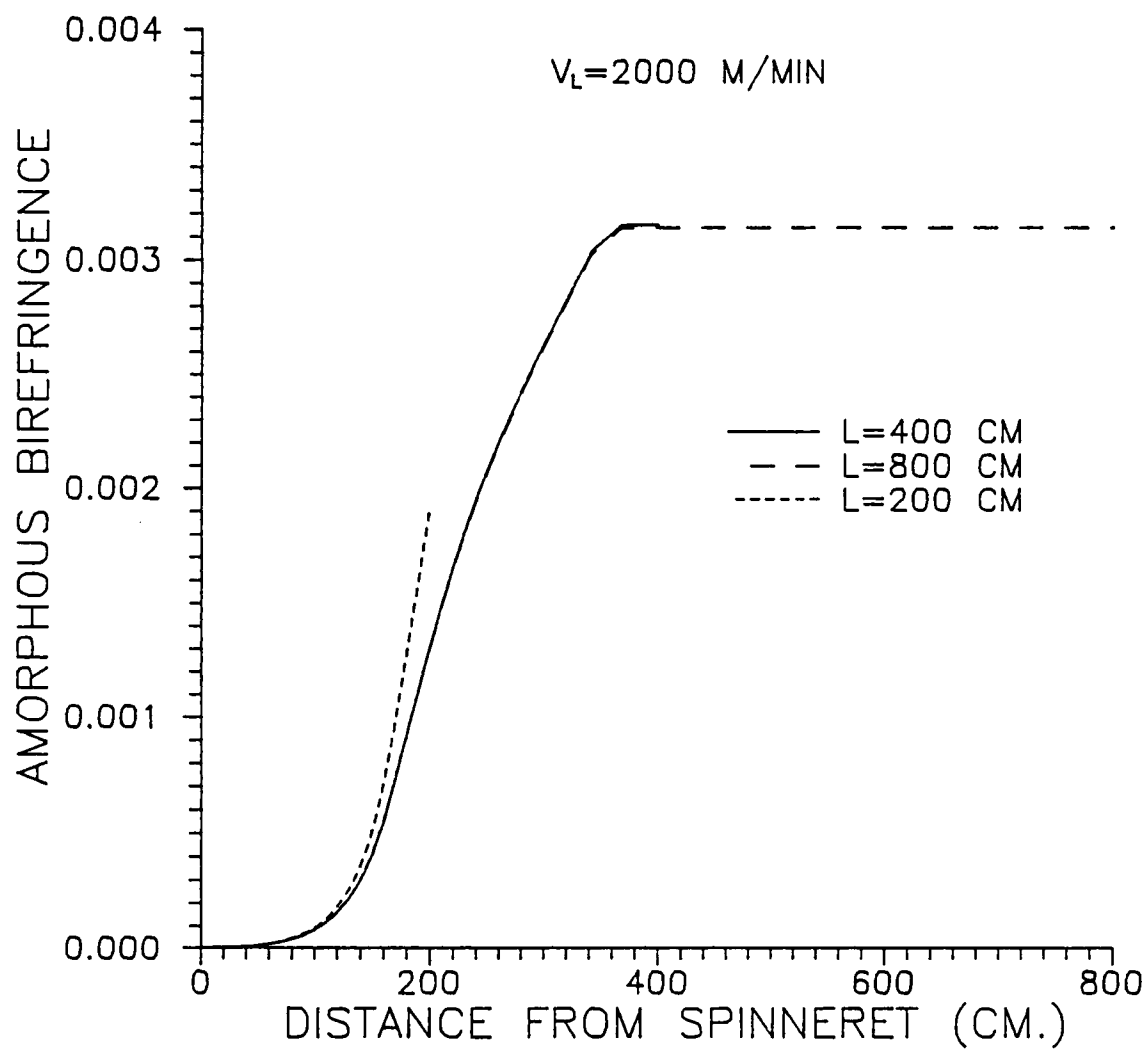


Figure 8.14. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for three different spinline lengths.

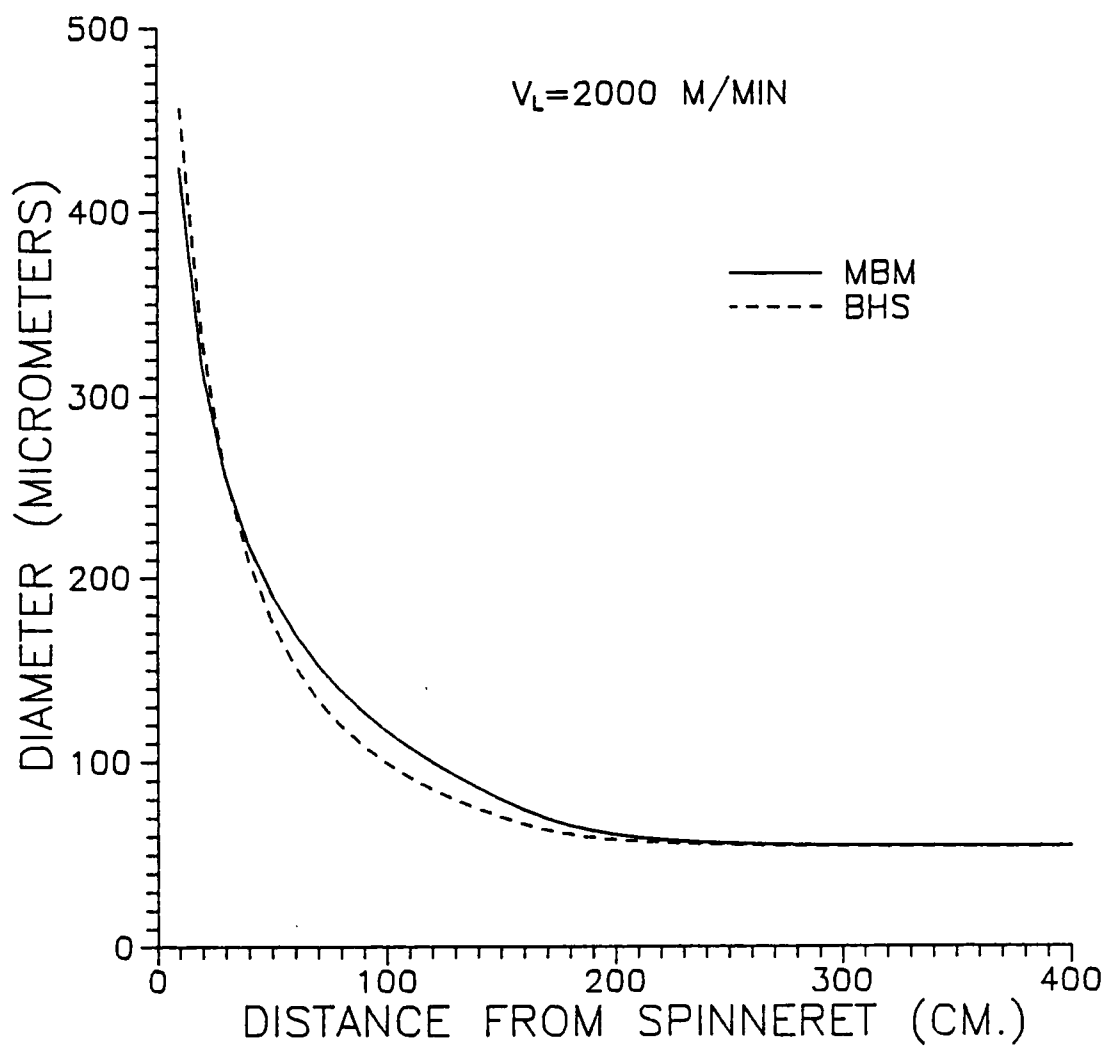


Figure 8.15. The predicted diameter profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for MBM and BHS resins.

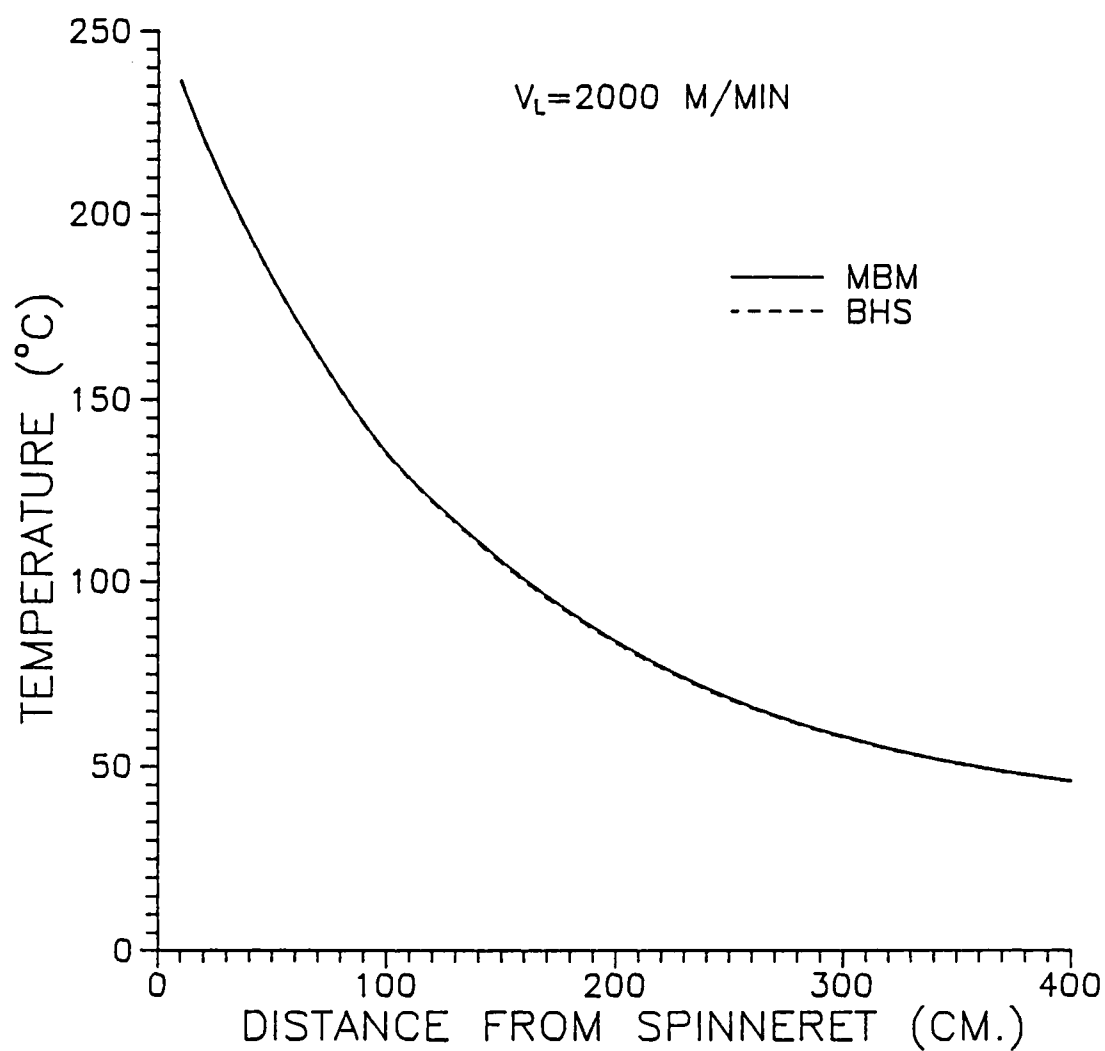


Figure 8.16. The predicted temperature profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for MBM and BHS resins.

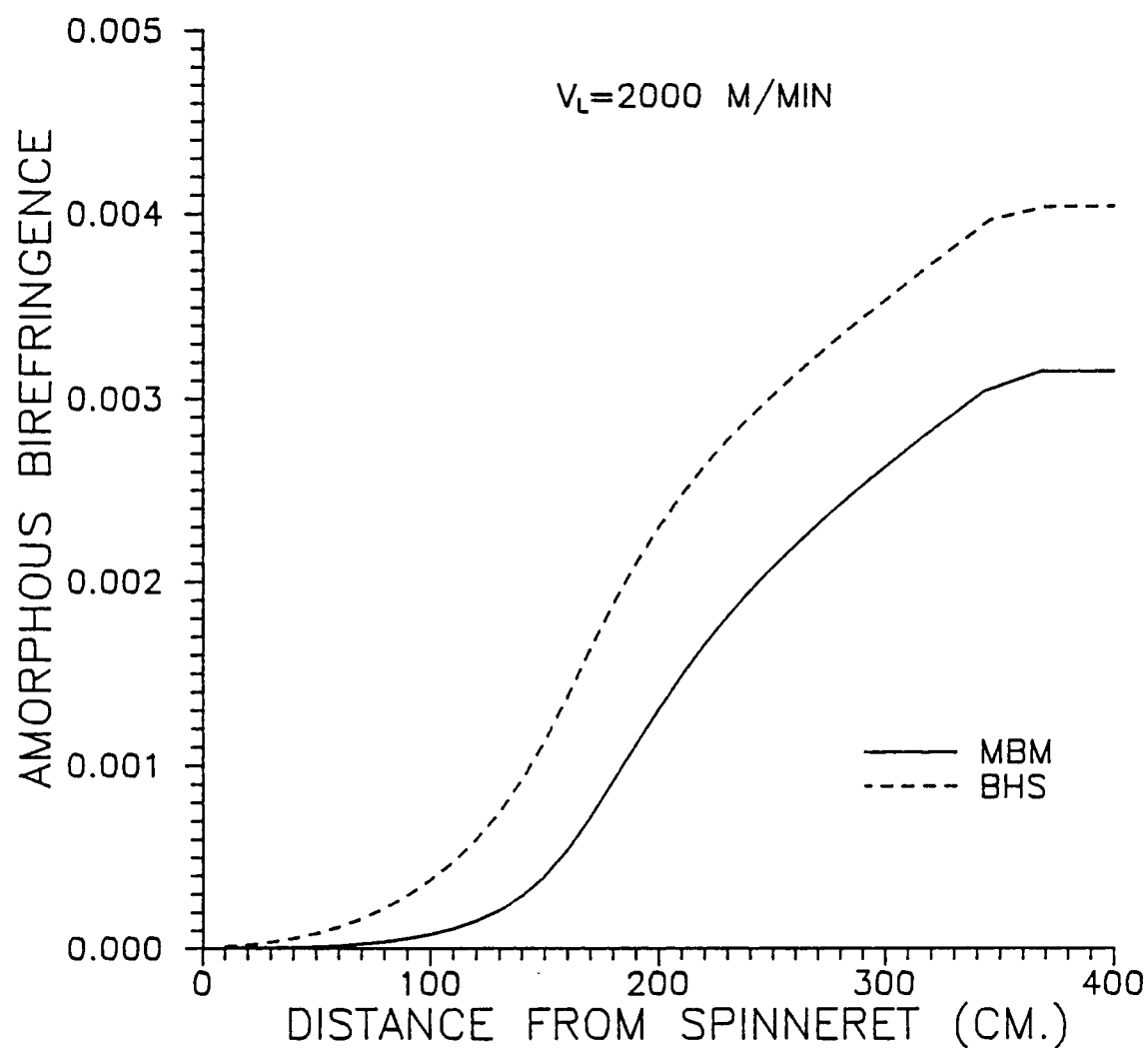


Figure 8.17. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for MBM and BHS resins.

to 8 meters. In fact, by increasing the spinline length from 4 meters to 8 meters, more stresses are developed on the spinline and it may lead to a breakage of the spinline. Note that the temperature profile is also sensitive to the cooling air temperature and flow rate. For the present calculations this was kept constant. More generally, as spinline length decreases, it is necessary to use more severe cooling conditions in order to achieve necessary cooling before reaching the first godet in the draw down device. Thus a more realistic calculations might be a comparison that maintains nearly the same temperatures at the end of the spinline.

The diameter, temperature and amorphous birefringence profiles for circular spinneret geometry are compared for MBM and BHS resins using identical process conditions (shown in Table 16) at take-up speed of 2000 m/min in Figures 8.15 to 8.17, respectively. Note that BHS resin had significantly higher spinline viscosity than MBM resin as can be seen from Figure 7.7. It can be seen from Figure 8.16 that the temperature profiles for BHS and MBM resin are identical. This is because the temperature profile depends mainly on throughput rate and at a given throughput rate, the temperature profile would be independent of resin type and take-up velocity. However, a faster draw down in diameter in the upper part of the spinline is obtained for BHS compared to MBM as can be seen from Figure 8.15. This is because BHS resin has a higher spinline viscosity than MBM resin. The higher viscosity of BHS also leads to higher spinline stresses and higher spun birefringence compared to MBM resin as can be seen from Figure 8.17. This would likely lead to a different level of post spinning draw needed to achieve the natural draw ratio of the filament (MBM would be somewhat higher than BHS).

In the case of industrial melt spinning, the spinneret shape can be different from

circular geometry. For example, trilobal filaments for making carpets are prepared from a "Y" shaped spinneret. Thus, it is important to predict and understand the spinline behavior for a spinneret having other than a circular shape. The diameter, temperature, and amorphous birefringence profiles for circular and triangular spinneret geometry are compared for throughput rate of 5 g/min and take-up velocity of 2000 m/min in Figures 8.18 to 8.20, respectively. Equivalent diameter is computed from the cross-sectional area of the triangular shape filaments. Thus the spun filaments of circular and triangular cross section would have the same as-spun filament denier. It can be seen from Figure 8.19 for temperature profile that the cooling is faster for triangular shape filament due to higher filament surface area than for circular filament. This leads to more draw down in the upper part of the spinline for the triangular shaped filament as compared to circular shaped filament as can be seen from Figure 8.18. This enhanced cooling for triangular shaped filament also leads to higher spinline stresses and higher amorphous birefringence along the spinline as compared to circular shape. This can be seen from Figure 8.20 for amorphous birefringence profile (which is proportional to stress profile) for circular and triangular shape filaments. It should be noted that it is the stress at freeze point and hence, the amorphous birefringence of the spun filament which governs the subsequent drawing behavior. In order to show the effect of filament cross-section shape on the stress-induced crystallization at high spinning speeds, simulation was carried out for triangular shaped spinneret at throughput rate of 5 g/min and take-up velocity of 6000 m/min. The temperature profiles for circular and triangular shaped spinneret of same cross-sectional area (with no shape change) at the take-up velocity of 6000 m/min are compared in Figure 8.21. It can be seen from Figure 8.21 that stress-induced crystallization was triggered closer to the spinneret for the triangular shaped spinneret compared to the circular shaped spinneret. This is again because lower spinline

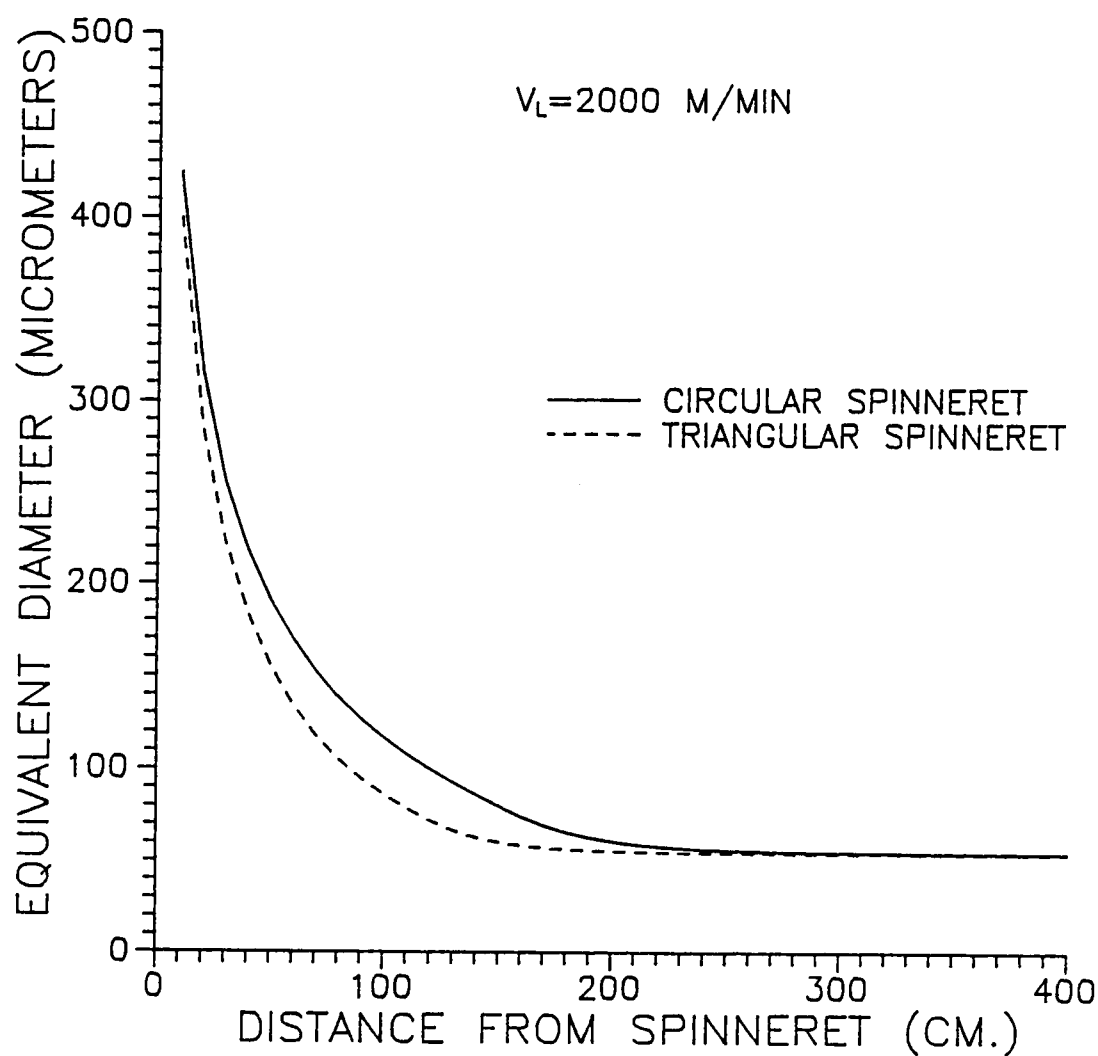


Figure 8.18. The predicted diameter profiles for circular and triangular filaments at throughput rate of 5 g/min and at take-up velocity of 2000 m/min.

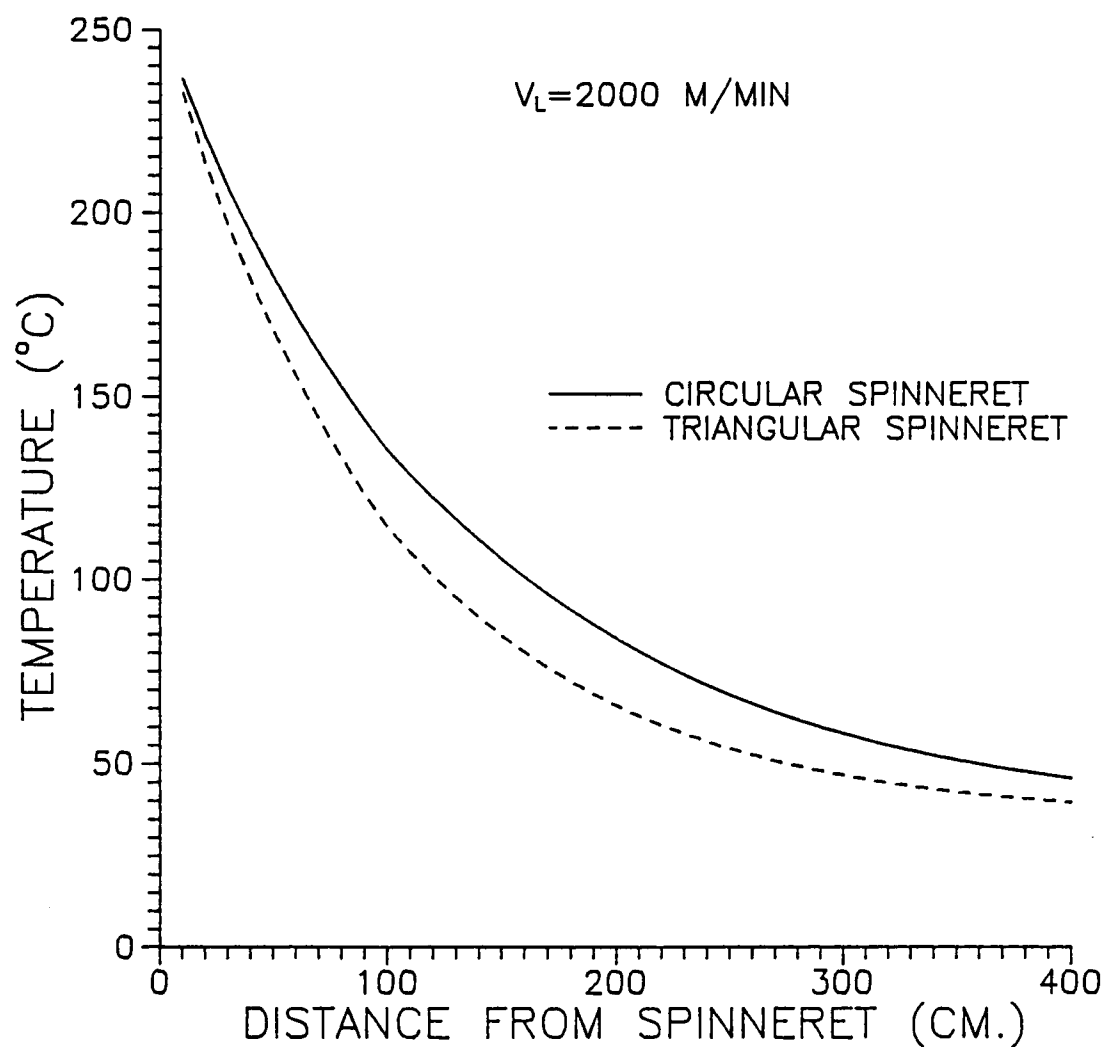


Figure 8.19. The predicted temperature profiles for circular and triangular filaments at throughput rate of 5 g/min and at take-up velocity of 2000 m/min.

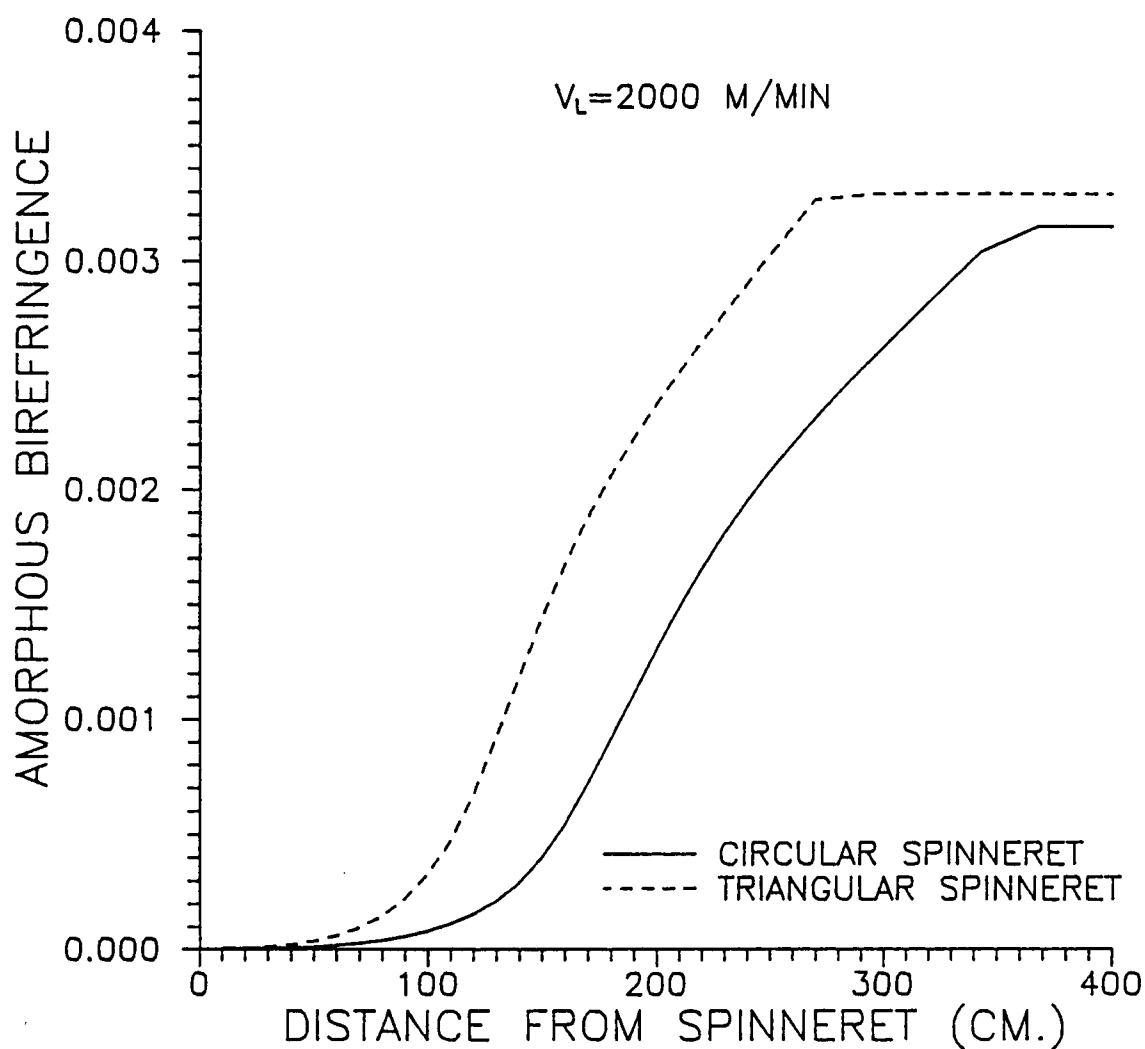


Figure 8.20. The predicted amorphous birefringence profiles for circular and triangular filaments at throughput rate of 5 g/min and at take-up velocity of 2000 m/min.

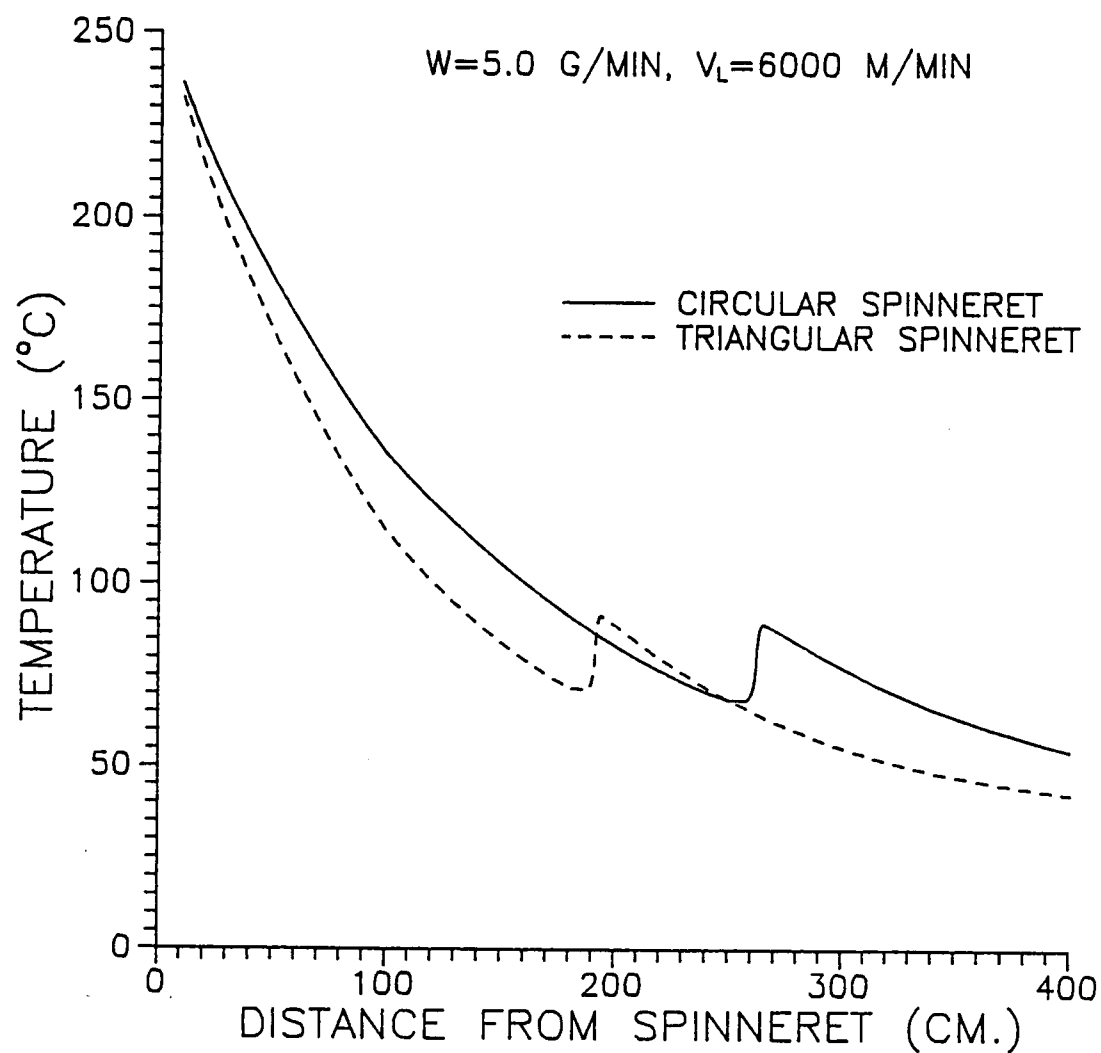


Figure 8.21. The predicted temperature profiles for circular and triangular shaped spinneret at the take-up velocity of 6000 m/min.

temperatures obtained for triangular shaped filaments leads to higher spinline stresses and thus, stress-induced crystallization will be triggered closer to the spinneret.

Multifilament melt spinning is the process used to produce fibers at the industrial level. During this process, a polymer is spun as a bundle of filaments with cross-flow quenching air to cool the filaments. The above work on modeling and computer simulation of nylon 6 melt spinning processes, however, deals with the situation where a single filament is being extruded from a spinneret. This implies that the quench conditions seen by all the filaments within a bundle are identical; hence there is no variation in spun fiber quality within a bundle. In actual practice, however, each row of filaments experiences different cooling conditions owing to the location of quench air supply. Both the quench air temperature and the quench air velocity are altered significantly as the air traverses the filament bundle. Two major sources of interaction occur. The hot filaments lose heat to the quench air and result in higher quench air temperature experienced by another filament. The second effect is due to downward drag of air by the moving filaments in the bundle, thereby reducing cross flow velocity for filaments further from the source of cooling air. Thus the quench air temperature velocity decreases and the air temperature increases as the air progresses through the bundle. Dutta (156) has presented a viable theoretical framework for the analysis of multifilament melt spinning. Such an analysis which would give quench air temperature and velocity profile across a bundle of filament is beyond the scope of the present work.

In order to estimate the significance of changes in quench conditions, a run was made for MBM resin and triangular geometry using quench air temperature of 40 °C (instead of 20 °C) and quench air velocity of 20 cm/s (instead of 40 cm/s). The diameter, temperature, and amorphous birefringence for both the quench conditions at the take-up

velocity of 2000 m/min are compared in Figures 8.22 to 8.24, respectively. It can be seen from Figure 8.23 that the somewhat higher spinline temperatures are obtained using higher quench air temperature and lower quench air velocity as expected. This leads to somewhat reduced draw down in diameter profile for the reduced quenching efficiency case as can be seen from Figure 8.22. The higher spinline temperatures leads to somewhat lower spinline stresses, and somewhat lower amorphous orientation for the reduced quenching efficiency case as can be seen from Figures 8.24. These calculations give an estimate of variabilities in spinline dynamics and spun birefringence due to variations in quench conditions.

It is a known fact that the spun birefringence of a nylon 6 filament determines its natural draw ratio. The stresses in the filament at the freeze point determines the spun birefringence in the case when no appreciable crystallization occurs on the spinline. The model can predict the stress and hence, birefringence of the spun filament at any set of process conditions. Experimentally, one can determine the maximum draw ratio that can be achieved for a filament spun under known set of conditions. Hence, using the computed spun birefringence, a correlation between computed spun birefringence and the draw ratio can be developed. Such a correlation would be very useful in determining the subsequent drawing conditions of the spun yarn. It can further be used to optimize the productivity and the properties of the drawn filaments.

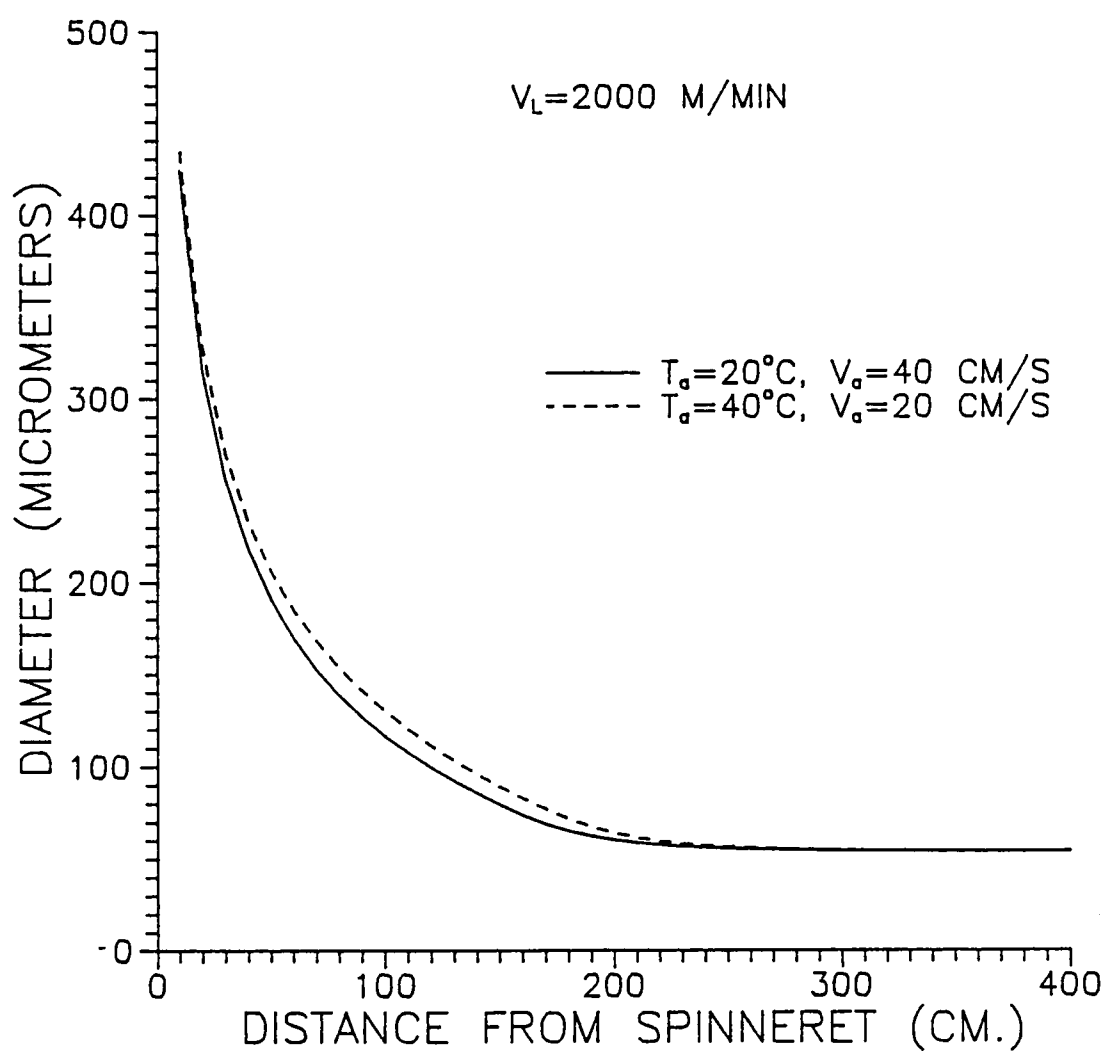


Figure 8.22. The predicted diameter profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for two different quench conditions.

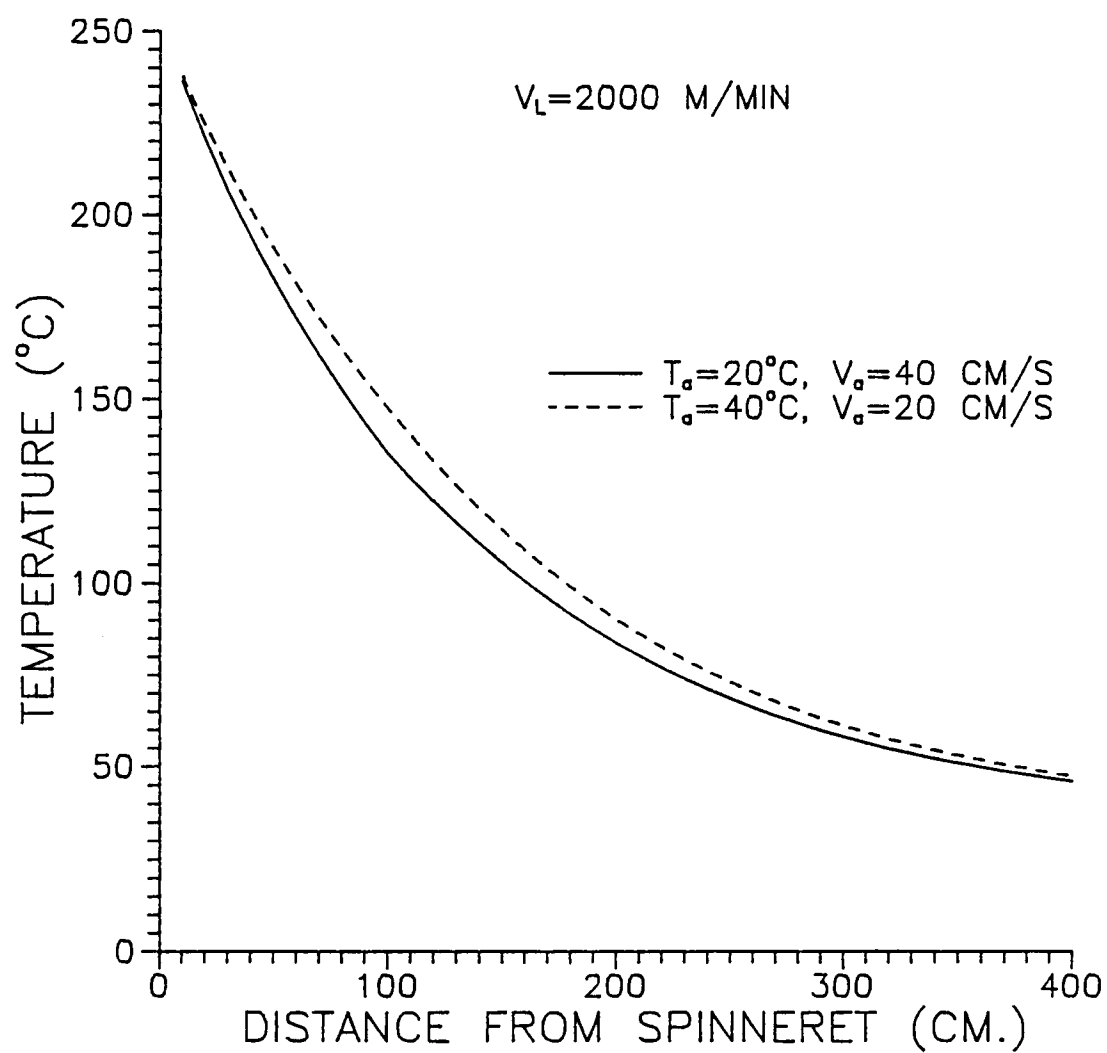


Figure 8.23. The predicted temperature profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for two different quench conditions.

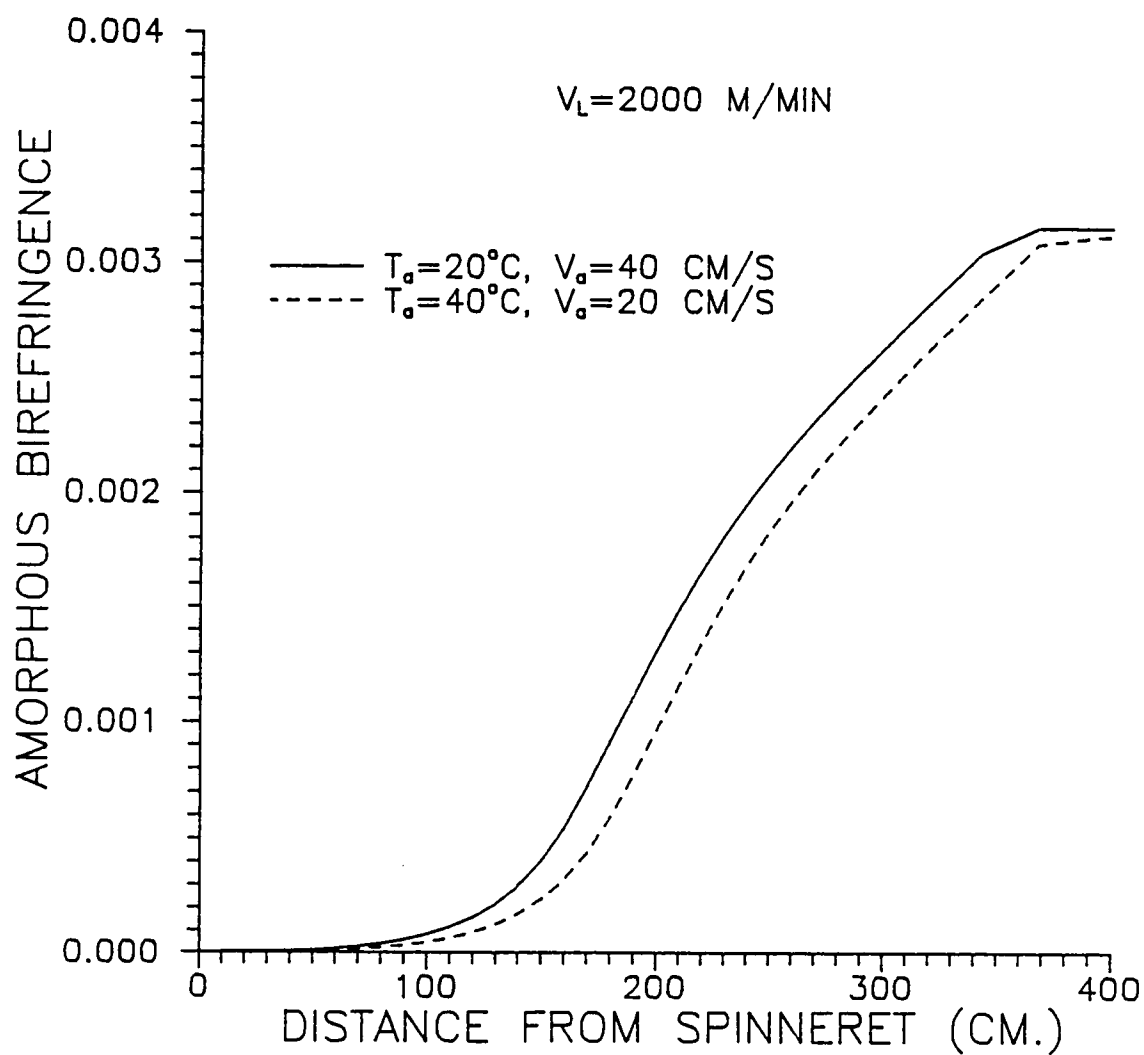


Figure 8.24. The predicted amorphous birefringence profiles for circular filament at throughput rate of 5 g/min and take-up velocity of 2000 m/min for two different quench conditions.

CHAPTER 9

CONCLUSIONS

Polymer melt spinning involves many interacting variables and hence, a mathematical model of the process is quite valuable not only for understanding the process but also for predicting spinline kinematics, dynamics and structure development under various process conditions. The basic purpose of this research was to examine the spinline model developed by Zieminski with the aim of providing an improved model and a better understanding of the polymer physics and polymer rheology underlying the model.

The modifications of the spinline model developed by Zieminski (13,14) were described earlier. These modifications led to a set of differential equations which could be solved and implemented on an IBM PC using the IBM Advanced BASIC interpreter (referred to as BASICA). The melt spinning model program can be executed much faster (in few minutes) using a suitable BASIC compiler such as TURBOBASIC or QBASIC and using a math coprocessor.

An inversion procedure is useful to obtain the apparent elongational viscosity function and heat transfer coefficient correlation for the melt spinning process. These are the key input relationships required by the model. The inversion procedure used by Bheda has been improved to give better results for elongation rates and hence, the apparent elongational viscosity data along the spinline. The improved inversion procedure as described earlier also gave better results for the heat transfer coefficient data along the spinline. The improved inversion procedure revealed the effects of polymer throughput rates and take-up speeds on the computed apparent elongational viscosity functions of CN 9984 resin and BHS resin from the experimental data obtained by

Bheda. The reason for the difference may be a result of experimental error in the tension measurements or the difference may also be because of viscous thinning and elastic effects in nylon 6 melt spinning. Since, the effects were not large, averaged viscosity functions were used in the spinline model calculations. The predictions of the improved spinline mathematical model compared well with the experimental data on CN 9984 and BHS resin obtained by Bheda.

The simulated and the experimental results provide understanding of the role of various process and resin variables in controlling the spinline dynamics and the structure and properties of melt spun filaments. The mathematical simulation and the experimental results make it quite clear that crystallization in the spinline is controlled by a competition between crystallization rates, which are largely controlled by the level of molecular orientation, and cooling rates, which is controlled by the mass flow rate, spinning speed and cooling medium. The balance of this competition determines whether crystallization will occur and the temperature at which it occurs. Increasing the mass throughput rate substantially reduces the polymer cooling rate and the spinline stress thereby moving the point at which crystallization begins further from the spinneret. Increasing the molecular weight causes crystallization to occur closer to the spinneret and at a higher temperature.

The present simulations could not predict the "necking" observed for BHS and CN 9984 resin at high speeds. Use of a suitable non-Newtonian (deformation-thinning) viscoelastic constitutive equation in a spinline model probably can explain such necking phenomena. Such a model is also necessary to explain the effects of throughput rate and take-up speeds on the apparent elongational viscosity function as shown by using improved inversion procedure on the results obtained by Bheda. A modified Cross model to describe temperature and instantaneous elongation rate dependent spinline

viscosity could not predict nylon 6 spinline rheological behavior. Even though the modified Cross model can predict the effects of throughput rate and take-up speeds through elongation rate dependent viscosity, it tends to predict excessive viscous-thinning compared to that obtained in the nylon 6 spinline. Hence, this type of rheological constitutive equation can not be used to describe nylon 6 spinning. The assumption of a Newtonian behavior is adequate to describe spinline rheological behavior for nylon 6 spinning.

The half-time analysis can be used to correlate and extrapolate the isothermal crystallization rates obtained over a narrow range of temperatures at low supercoolings. Based on the study described earlier, it can be concluded that neither the Nakamura model nor the empirical Kamal model can quantitatively predict the quiescent nonisothermal crystallization curves using crystallization rates measured under isothermal conditions. However, the Nakamura model gives substantially better predictions of nonisothermal data than the Kamal model. The Kamal model is fundamentally not of correct functional form as crystallization rate depends on an ambiguous residence time which is also difficult to evaluate in a polymer processing operation. The non-linear regression method described earlier can be used to fit nonisothermal data directly using the simplified differential form of Nakamura model to obtain the crystallization rate equation parameters $(1/t_{1/2})_0$ and C_3 . The extended half-time analysis to include orientation effects could not even qualitatively predict the on-spinline crystallization of BHS nylon 6 resin. This may be an indication of the failure of classical nucleation and growth theory under extreme conditions of high stress and high supercoolings. The empirical Ziabicki factor $\exp(Af_a^2)$ at least semi-quantitatively described the nylon 6 on-line crystallization.

Crystallization rates under stress and the effect of crystallinity on viscosity are still

major areas of uncertainty in developing a better model for high speed melt spinning. The present equations for dealing with stress induced crystallization are empirical and are based on an average value of amorphous orientation in a melt. Thus, they neglect the orientation distribution of amorphous segments and the depletion of oriented segments during crystallization. The assumption of a Newtonian behavior is adequate to describe spinline rheological behavior for nylon 6 spinning. However, the Newtonian assumption may not be adequate to describe spinline rheological behavior of highly viscous thinning polymers such as polypropylene and high density polyethylene or of highly elastic polymers such as low density polyethylene. In such cases a non-Newtonian inelastic (e.g. modified Cross model) or non-Newtonian viscoelastic (e.g. Bogue-White or PTT model) rheological constitutive equation might be necessary to describe spinline rheological behavior. The accurate description of spinline rheological behavior is also necessary to describe subsequent stress-induced crystallization in the spinline. For such cases, if major differences in the apparent elongational viscosity data at different spinline processing conditions are obtained then it may be necessary to use a more complex rheological constitutive equation in the spinline model .

LIST OF REFERENCES

LIST OF REFERENCES

1. R. A. Brooman, English Patent 10,582 (1845).
2. W. H. Carothers and J. W. Hill, J. Amer. Chem. Soc., 54, 1579 (1932).
3. W. H. Carothers, DuPont, U.S. Patent 2,130,948 (1938); DuPont, U.S. Patent 2,137,235 (1938); DuPont, U.S. Patent 2,157,116 (1938).
4. H. H. George, Polym. Eng. Sci., 22, 292 (1982).
5. S. Kase and T. Matsuo, J. Text. Mach. Soc., Japan, 18, 188 (1965).
6. S. Kase and T. Matsuo, J. Polym. Sci., A3, 2541 (1965).
7. S. Kase and T. Matsuo, J. Appl. Polym. Sci., 11, 251 (1967).
8. A. Prastaro and P. Parrini, Text. Res. J., 45, 118 (1975).
9. H. Yasuda, H. Sugiyama and Y. Yanagawa, Sen-i-Gakkaishi, 35, 370 (1979).
10. D. K. Gagon and M. M. Denn, Polym. Eng. Sci., 21,, 844 (1981).
11. H. Yasuda, H. Sugiyama and S. Hayashi, Sen-i-Gakkaishi, 40, 227 (1984). Ibid., p.488.
12. A. Dutta and V. M. Nadkarni, Text. Res. J., 54, 35 (1984).
13. K. F. Zieminsky and J. E. Spruiell, J. Appl. Polym. Sci., 35, 2223 (1988).
14. K. F. Zieminsky, Ph.D. dissertation, University of Tennessee, Knoxville, June 1986.
15. J. Shimizu, N. Okui and T. Kakutani, in "High Speed Fiber Spinning", A. Ziabicki and H. Kawai Eds, John Wiley and Sons, New York (1985).
16. K. Katayama and M-G. Yoon, in "High Speed Fiber Spinning"; Wiley, New York, 1985, p.207.
17. J. H. Bheda, Ph.D. Dissertation, University of Tennessee, March (1987).
18. J. H. Bheda and J. E. Spruiell, J. Appl. Polym. Sci., 39, 447 (1990).
19. H. H. George and M. H. G. Deeg, Paper presented at the second annual meeting of the International Polymer Processing Society, Montreal, Canada (1986).
20. J. Zhou, M.S. Thesis, University of Tennessee (1988).
21. A. Ziabicki, "Fundamentals of Fiber Formation", Wiley, London (1976).

22. C. D. Han, "Rheology in Polymer Processing", Academic Press, New York (1976).
23. B. C. Sakiadis, AIChE J., 7, 467 (1961).
24. M. Matsui, Trans. Soc. Rheol., 20, 465 (1976).
25. J. Shimizu, N. Okui and K. Tamai, Sen-I Gakkaishi, 39, 398 (1983).
26. S. Middleman, in "Fundamentals of Polymer Processing", McGraw-Hill, New York (1977).
27. C. D. Denson, Polym. Eng. Sci., 13, 125 (1973).
28. M. Van Den Tempel, The Chemical Engineer, P.95, Feb (1977).
29. F. C. Frank, Proc. Roy. Soc., A319, 127 (1970).
30. F. Trouton, Proc. Roy. Soc. (London), A, 77, 426 (1906).
31. L. E. Nielsen, "Polymer Rheology", Marcel Dekker Inc., New York (1977).
32. R. M. Patel, M.S. Thesis, University of Tennessee, Knoxville,
33. R. M. Patel and D. C. Bogue, J. Rheol., 33(4), 607 (1989).
34. C. J. S. Petrie, "Elongation Flows", Pitman, London (1979).
35. M. Matsui and D. C. Bogue, Polym. Eng. Sci., 16(11), 735 (1976).
36. J. D. Tsou and D. C. Bogue, J. Non-Newtonian Fluid Mech., 17, 331 (1985).
37. J. G. Oldroyd, Proc. Roy. Soc., A77, 426 (1950).
38. J. G. Oldroyd, Proc. Roy. Soc., A200, 523 (1958).
39. W. Prager, "Introduction to Mechanics of Continua", Chicago, Ginn, P.155 (1961).
40. S. Ramachandran, H. W. Gao and E. B. Christiansen, Macromolecules, 18, 695 (1985).
41. B. L. Lee and J. L. White, Trans. Soc. Rheol., 18, 467 (1974).
42. A. Ziabicki, J. Non-Newtonian Fluid Mech., 30, 141 (1988).
43. D. C. Bogue, Ind. Eng. Chem. Fund., 5, 253 (1966).
44. D. C. Bogue and J. L. White, "engineering Analysis of Non-Newtonian Fluid", NATO Agardograph, #144 (1970).
45. S. Middleman, Trans. Soc. Rheol., 13, 123 (1969).

46. I-Jen Chen and D. C. Bogue, *Trans. Soc. Rheol.*, 16, 59 (1972).
47. I-Jen Chen, G. E. Hagler, L. E. Abbott, D. C. Bogue and J. L. White, *Trans. Soc. Rheol.*, 16, 473 (1972).
48. I. Furuta, V. M. Lobe and J. L. White, *J. Non-Newtonian Fluid Mech.*, 1, 207 (1976).
49. Y. Ide and J. L. White, *J. Appl. Polym. Sci.*, 22, 1061 (1978).
50. T. Takaki and D. C. Bogue, *J. Appl. Polym. Sci.*, 19, 419 (1975).
51. L. W. Morland and E. H. Lee, *Trans. Soc. Rheol.*, 4, 233 (1960).
52. H. Markovitz, *J. Polym. Sci. Polym. Symp.*, 50, 431 (1975).
53. B. Bernstein, E. A. Kearsley and L. A. Zapas, *Trans. Soc. Rheol.*, 7, 391 (1963).
54. G. Marrucci, *Trans. Soc. Rheol.*, 16, 321 (1972).
55. N. B. Bekkedahl, *J. Res. Natl. Bur. Std.*, 13, 411 (1934).
56. L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York (1964).
57. D. W. Van Krevelen, "Properties of Polymers", Elsevier, Amsterdam (1976).
58. J. D. Hoffman and J. I. Lauritzen, *J. Res. Natl. Bur. Std.*, A, 65, 297 (1961).
59. J. D. Hoffman and J. Weeks, *J. Chem. Phys.*, 37, 1723 (1962).
60. J. D. Hoffman, *SPE Trans.*, 4, 315 (1964).
61. J. D. Hoffman, G. T. Davis and J. I. Lauritzen, in "Treatise on solid state chemistry: crystalline and non-crystalline solids, J. B. Hannay, Ed., Vol 3, Chap. 7, Plenum, New York (1976).
62. A. S. Kenyon, R. C. Gross and A. L. Wurstner, *J. Polym. Sci.*, 40, 159 (1959).
63. L. Mandelkern, N. L. Jain and H. Kim, *J. Polym. Sci., Part A-2*, 6, 165 (1968).
64. T. Suzuki and A. J. Kovacs, *Polymer J.*, 1, 82 (1970).
65. A. N. Kolmogoroff, *Isvest. Akad. Nauk SSSR Ser. Math.*, 1, 335 (1937).
66. W. A. Johnson and R. T. Mehl, *Trans. AIME*, 135, 416 (1939).
67. M. Avrami, *J. Chem. Phys.*, 7, 1103 (1939); 8, 212 (1940); 9, 177 (1941).
68. U. R. Evans, *Trans. Faraday Soc.*, 41, 365 (1945).

69. L. Mandelkern, F. A. Quinn, Jr., P. L. Flory, J. Appl. Phys., 25, 830 (1954).
70. B. Wunderlich, "Macromolecular Physics, Vol. 2", Academic press, New York (1976).
71. Y. P. Khanna and T. J. Taylor, Polym. Eng. Sci., 28, 1042 (1988).
72. W. Banks, M. Gordon, R. J. Roe and A. Sharples, Polymer, 4, 61 (1963).
73. F. P. Price, J. Polym. Sci., Part A, 3, 3079 (1965).
74. I. H. Hillier, J. Polym. Sci., Part A, 3, 3067 (1965).
75. A. Booth and J. N. Hay, Polymer, 12, 365 (1972).
76. C. Velisaris and J. Seferis, Polym. Eng. Sci., 26, 1574 (1986).
77. W. Dietz, Colloid and Polym. Sci., 259, 413 (1981).
78. P. Cebe, Polym. Eng. Sci., 28, 1192 (1988).
79. P. Archambault and R. E. Prud'homme, J. Polym. Sci., Polym. Phys. ed., 18, 35 (1980).
80. A. Hammami, M.S. Thesis, University of Tennessee, Knoxville (1990).
81. K. Nakamura, K. Katayama and T. Amano, J. Appl. Polym. Sci., 17, 1031 (1973).
82. T. Ozawa, Polymer, 12, 150 (1971).
83. W. J. Kozlowski, J. Polym. Sci., Part C, 38, 47 (1972).
84. M. Eder and A. Wlochowicz, Polymer, 24, 1593 (1983).
85. B. Monasse and J. M. Haudin, Colloid and Polym. Sci., 264, 117 (1986).
86. L. C. Lopez and G. L. Wilkes, Polymer, 30, 882 (1989).
87. M. R. Kamal and E. Chu, Polym. Eng. Sci., 23, 27 (1983).
88. P. J. Flory, J. Chem. Phys., 15, 397 (1947).
89. K. Kobayashi and T. Nagasawa, J. Macromol. Sci. (B), 4, 331 (1970).
90. A. Ziabicki, Polimery, 18, 615 (1973).
91. K. J. Smith Jr., A. Green and A. Ciferri, Kolloid Z., 194, 49 (1964).
92. W. R. Krigbaum, J. W. Dawkins, G. H. Via and Y. I. Balta, J. Polym. Sci. (A-2), 4, 475 (1966).

93. J. W. Haas and B. Maxwell, *J. Appl. Polym. Sci.*, 14, 2407 (1970).
94. A. Peterlin, *Polym. Prepr.*, 16, 315 (1975).
95. V. G. Baranov, *Discuss. Faraday. Soc.*, 49, 137 (1970).
96. J. H. Southern and R. S. Porter, *J. Appl. Polym. Sci.*, 14, 2305 (1970).
97. W. R. Krigbaum and R. J. Roe, *J. Polym. Sci. (A-2)*, 2, 4391 (1964).
98. R. Oono, K. Miyasata and K. Ishikawa, *J. Polym. Sci. (Polym. Phys. Edn)*, 11, 1477 (1973).
99. R. S. Stein and J. T. Judge, *J. Appl. Phys.*, 32, 2357 (1961).
100. W. J. Dunning, *Trans. Faraday Soc.*, 50, 1115 (1954).
101. A. Ziabicki, *Colloid Polym. Sci.*, 252, 207 (1974).
102. J. R. Katz, *Kolloid Z.*, 36, 300 (1925).
103. L. R. G. Treloar, *Trans. Faraday Soc.*, 37, 84 (1941).
104. A. N. Gent, *Trans. Faraday Soc.*, 8, 369 (1954).
105. H. G. Kim and L. Mandelkern, *J. Polym. Sci.*, 6, 181 (1968).
106. T. Kawai, T. Matsumoto, M. Kato and H. Maeda, *Kolloid Z.*, 222, 1 (1968).
107. A. J. Pennings and M. F. J. Pijpers, *Macromolecules*, 3, 261 (1970).
108. A. J. Pennings, J. M. A. A. Van der Mark and H. C. Booji, *Kolloid Z.*, 236, 99 (1970).
109. G. C. Alfonso, M. P. Verdoni and A. Wasiak, *Polymer*, 19, 711 (1978).
110. C. C. Bai, Ph.D. dissertation, University of Tennessee, Knoxville (1984).
111. J. R. Dees and J. E. Spruiell, *J. Appl. Polym. Sci.*, 18, 1053 (1974).
112. L. R. G. Treolar, "Physics of Rubber elasticity", 2nd ed., Oxford Univ. Press, London and New York (1958).
113. J. E. Spruiell and J. L. White, *Polym. Eng. Sci.*, 15, 660 (1975).
114. A. M. Sharger, in "Elementary Metallurgy and Metallography," 2nd ed., Dover, New York (1961).
115. L. H. Van Vlack, in "Elements of Material Science," 2nd ed., Addison-Wesley, Reading, Mass. (1964).

116. J. C. Maxwell, *Proc. Roy. Soc.*, 22, 46 (1873).
117. W. Kuhn and F. Grun, *Kolloid Z.*, 101, 248 (1943).
118. T. Matsumoto and D. C. Bogue, *J. Polym. Sci., Polym. Phys. Eds.*, 15, 1663 (1977).
119. A. Wasiak and A. Ziabicki, A.C.S. Symposium on Fiber and Yarn processing, Philadelphia, Pa., April 1975; *Appl. Polymer Symposia*, 27, 111 (1975).
120. A. Ziabicki, *Kolloid Z.*, 167, 132 (1959).
121. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, 2, 14 (1959).
122. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, 6, 111 (1962).
123. W. C. Sheehan and T. B. Cole, *J. Appl. Polym. Sci.*, 8, 2359 (1964).
124. S. E. Ross, *J. Appl. Polym. Sci.*, 9, 2729 (1965).
125. K. Katayama, T. Amano and K. Nakamura, *Kolloid Z.*, 226, 125 (1968).
126. H. P. Nadella, M. M. Henson, J. E. Spruiell and J. L. White, *J. Appl. Polym. Sci.*, 21, 3003 (1977).
127. H. M. Heuvel and R. Huisman, *J. Appl. Polym. Sci.*, 22, 2229 (1978).
128. J. Shimizu, K. Toriumi and K. Tamai, *Sen-I-Gakkaishi*, 33, T-208 (1977).
129. J. Shimizu, N. Okui, T. Kikutani and K. Toriumi, *Sen-I-Gakkaishi*, 34, T-93 (1978).
130. J. Shimizu, N. Okui, A. Kaneko and K. Toriumi, *Sen-I-Gakkaishi*, 34, T-64 (1978).
131. Fu-Min Lu and J. E. Spruiell, *J. Appl. Polym. Sci.*, 34, 1521 (1987); *J. Appl. Polym. Sci.*, 34, 1541 (1987).
132. I. Hamana, M. Matsui and S. Kato, *Milliand Textilberichte*, 50, 382 (1969).
133. G. Vassilatos, B. H. Knox, H. R. E. Frankfort, in "High Speed Fiber Spinning", ed. A. Ziabicki and H. Kawai, Wiley, New York, 1985, p.383.
134. T. Kikutani, Ph.D. dissertation, Tokyo Institute of Technology, (1982).
135. R. J. Fisher and M. M. Denn, *AIChE J.*, 23, 23 (1977).
136. D. Acierno, J. N. Dalton, J. M. Rodriguez and J. L. White, *J. Appl. Polym. Sci.*, 15, 2395 (1971).

137. N. Hajji, Ph.D. Proposal, The University of Tennessee, Knoxville, May (1989).
138. Z. Kemblowski and J. Torzecki, *Rheo. Acta*, 22, 186 (1983).
139. R. Pflueger, in *Polymer Handbook*, ed. J. Brandrup and E. H. Immergut, Wiley-Interscience, New York (1975).
140. B. B. Burnett and W. F. McDevit, *J. Appl. Phys.*, 28, 1101 (1957).
141. J. H. Magill, *Polymer*, 3, 655 (1962).
142. A. Constantinides, in "Applied Numerical Methods with Personal Computers," McGraw-Hill, New York (1987).
143. E. Cernia and W. Conti, *J. Appl. Polym. Sci.*, 17, 3637 (1973).
144. J. W. Hill and J. A. Cuculo, *J. Appl. Polym. Sci.*, 18, 2569 (1974).
145. M. Inoue, *J. Polym. Sci., A-1*, 2013 (1963).
146. U. Gaur, S-F Lau, B. B. Wunderlich and B. Wunderlich, *J. Phys. Chem. Ref. Data*, 12, 65 (1983).
147. K. Matsumoto and M. Kiyodu, *Sen-I Gakkaishi*, 32, 365 (1976).
148. R. M. Patel and J. E. Spruiell, Unpublished results, University of Tennessee, Knoxville (1990).
149. R. M. Patel, J. H. Bheda and J. E. Spruiell, *J. Appl. Polym. Sci.*, 42, 1671 (1991).
150. H. H. George, in "High Speed Fiber Spinning"; ed. A. Ziabicki and H. Kawai, Wiley, New York, p.217. (1985).
151. A. YA. Malkin, V. P. Beghishev, I. A. Keapin and S. A. Bolgov, *Polym. Eng. Sci.*, 24, 1396 (1984).
152. J. R. Green, "Statistical Treatment of Experimental Data", Elsevier Scientific Pub. Co. (1977).
153. A. I. Isayev, M. Sobhanie, and J. S. Deng, *Rubber Chem. and Tech.*, 61, 906 (1988).
154. M. M. Cross, in "Polymer Systems: Deformation and Flow"; eds. Welton and Whorlow, Macmillan, London (1968).
155. N. Phan-Thien, *J. Rheology*, 22, 259 (1978).
156. A. Dutta, *Polym. Eng. Sci.*, 27, 1050 (1987).

APPENDIX

APPENDIX

Formulation of Non-Newtonian Inelastic and Non-Newtonian Viscoelastic Analysis of Melt Spinning

The assumption of Newtonian rheological behavior for nylon 6 spinline model seems to be accurate based on analysis of CN 9984 and BHS resin data obtained by Bheda. The temperature has a predominant effect on viscosity and hence, Newtonian assumption is justifiable. However, as shown earlier, even for highly Newtonian polymer melts such as nylon 6 there seems to be minor differences in the apparent elongational viscosity data at different throughput rates and at different take-up speeds. Such differences may be significant in case of melt spinning of polypropylenes and polyethylenes. In such cases, one may have to consider a non-Newtonian inelastic (viscous-thinning) or non-Newtonian viscoelastic constitutive equation to describe spinline rheological behavior. Accurate description of spinline rheological behavior is essential as predicted stresses subsequently affects the computation of stress-induced crystallization in a spinline model.

A general non-Newtonian inelastic equation that can be considered is a modified Cross model (153,154) which falls under the class of generalized power-law equation. The Cross model is very similar to the Bogue-White model for deformation rate dependent relaxation time. The modified Cross model with viscosity as a function of both temperature and deformation rate can be written as follows:

$$\eta(T) = \frac{\eta_o(T)}{1 + \left(\frac{\eta_o(T)}{G} \langle \pi_d^{1/2} \rangle \right)^b} \quad [1]$$

where "b" is an adjustable factor to obtain correct asymptotic slope of viscosity-shear rate curve at large shear rates. $\langle \pi_d \rangle$ is the second invariant of the deformation rate tensor. In simple shear, $\langle \pi_d^{1/2} \rangle$ is just the shear rate $\dot{\gamma}$, while in uniaxial elongation, it is $\sqrt{3} \cdot E$, where E is the elongation rate. The temperature dependent zero-shear viscosity $\eta_0(T)$ can be taken to be of Arrhenius form or of WLF form near T_g . For Arrhenius temperature dependence, $\eta_0(T) = K \exp(B/T)$ where parameters K and B can be obtained from zero-shear viscosity data at different temperatures. The adjustable parameters "b" and G (which can roughly be considered as shear modulus) can be obtained by fitting viscosity-shear rate curve at different temperatures. The modified Cross model has been used in simulation of injection molding of thermoplastics (153). The modified Cross model is an inelastic model with no memory effects. Note that at a given temperature, at low shear rates the viscosity approaches η_0 (zero-shear viscosity) and at high shear rates, power-law behavior is obtained.

The modified Cross model was used in the melt spinning model for nylon 6 to describe spinline rheological behavior. It could predict the effects of throughput rate and take-up speeds on the apparent spinline elongational viscosity data through temperature and elongation rate dependent viscosity. However, the modified Cross model tends to predict excessive viscous-thinning at higher take-up speeds than obtained in the nylon 6 spinline thereby giving poor fits to the diameter profile data. Also, there still remains a fundamental problem of whether simple shear data can be used to predict elongational flow data. Such generalized power-law equations may also not be suitable for predicting elongational flow behavior.

Since, polymer melts are viscoelastic, a viscoelastic constitutive equation using temperature dependent linear relaxation spectrum data should be used to describe spinline

rheological behavior. The formulation of viscoelastic analysis of nonisothermal melt spinning can be derived as shown below.

For viscoelastic analysis, the differential force balance needs to be obtained in terms of axial stress, σ_{11} . At steady state, differential force balance for melt spinning is as follows:

$$\frac{dF_{\text{rheo}}}{dz} = w \frac{dV}{dz} + 0.5 \rho_a C_d V^2 \pi D - \frac{w g}{V} \quad [2]$$

where g is the acceleration due to gravity, C_d is the drag coefficient, ρ_a is the density of air and w is the mass throughput rate.

However, using steady state equation of conservation of mass,

$$F_{\text{rheo}} = \sigma_{11} \left(\frac{\pi D^2}{4} \right) = \sigma_{11} \left(\frac{w}{V \rho} \right) \quad [3]$$

where ρ is the density of polymer melt and σ_{11} is the axial stress.

$$\text{So} \quad \frac{d}{dz} \left(\sigma_{11} \frac{w}{V \rho} \right) = \frac{w}{V \rho} \frac{d\sigma_{11}}{dz} - \sigma_{11} \frac{w}{\rho V^2} \frac{dV}{dz} \quad [4]$$

Equating [2] and [4] and rearranging, we get differential force balance in terms of axial stress as follows:

$$\frac{d\sigma_{11}}{dz} = \rho V \frac{dV}{dz} + 2 \rho_a C_d \frac{V^2}{D} - \rho g + \frac{\sigma_{11}}{V} \frac{dV}{dz} \quad [5]$$

The differential equations for extra stress tensors T_{11} and T_{22} for Bogue-White model or Phan-Thien and Tanner (PTT) model (155) using single relaxation time and relaxation modulus for steady melt spinning (one-dimensional) flow are as follows:

$$\frac{dT_{11}}{dz} = \left[\frac{2}{V} \frac{dV}{dz} - \frac{1}{V \tau_{\text{eff}}} \right] T_{11} + \frac{2G}{V} \frac{dV}{dz} \quad [6]$$

$$\frac{dT_{22}}{dz} = \left[-\frac{1}{V} \frac{dV}{dz} - \frac{1}{V \tau_{\text{eff}}} \right] T_{11} - \frac{G}{V} \frac{dV}{dz} \quad [7]$$

where G is a shear modulus and τ_{eff} is an effective relaxation time (deformation rate dependent) which for Bogue-White model is

$$\tau_{\text{eff}} = \frac{\tau(T)}{1 + (a \tau \sqrt{3} E)^n} \quad [8]$$

and for PTT model is

$$\tau_{\text{eff}} = \frac{\tau(T)}{1 + \left[\frac{\alpha}{G} (T_{11} + T_{22} + T_{33}) \right]} \quad [9]$$

where τ is a relaxation time under equilibrium, "a" is a thinning parameter and α is an adjustable parameter for elongational flows. α is related to stress saturation in uniform, uniaxial tension at high extension rates. α has been measured only for low density polyethylene, for which reported value is 0.015 (155). For melt spinning, T_{22} and T_{33} are equal to each other. Note that the PTT model given above assumes a shear parameter ζ to be zero. The temperature dependence of stress is contained in the parameters τ and G . The equilibrium relaxation time τ is a function of temperature which using the assumption of thermorheological simplicity can be taken to be of Arrhenius form or WLF form. For $a=\alpha=0$, the upper convected Maxwell model is obtained.

Noting that $\sigma_{11} = T_{11} - T_{22}$, after subtracting equation [7] from [6] and equating with equation [5], one can get equation for dV/dz as follows:

$$\frac{dV}{dz} = \frac{\rho V g - 2 \rho_a C_d \frac{V^3}{D} - \frac{\sigma_{11}}{\tau_{eff}}}{\rho V^2 + (\sigma_{11} - 2T_{11} - T_{22} - 3G)} \quad [10]$$

Hence, in the viscoelastic modeling of melt spinning, differential equations [6], [7], [10], the differential equation for energy balance and the differential equation for crystallization kinetics (Nakamura model) would form the set of simultaneous first order differential equation to be solved numerically. Additional initial conditions on extra stress tensors T_{11} and T_{22} are also required for the viscoelastic fluids. One possible boundary conditions for T_{11} and T_{22} can be $T_{11} = \sigma_{11}$ and $T_{22} = 0$.

For non-Newtonian inelastic modeling of melt spinning, differential force balance equation [2] (or [5]), an equation for $dV/dz = \sigma_{11}/\eta_{eapp}(T, E)$ (E =elongation rate), the differential equation for energy balance and the differential equation for crystallization kinetics (Nakamura model) would form the set of simultaneous first order differential equation to be solved numerically. For Newtonian modeling of melt spinning, Newton's law of viscosity $dV/dz = \sigma_{11}/\eta_{eapp}(T)$ is used.

VITA

Rajen M. Patel was born in Ahmedabad, India on June 4, 1963. He graduated from Jai Hind College, Bombay in June 1980 with science major. He entered the University of Bombay, Department of Chemical Engineering in July of 1980. He received the Bachelor of Science degree in Chemical Engineering with first class with Distinction in July, 1984. After working for a year in Bombay, he joined the Polymer Engineering department at the University of Tennessee, Knoxville for graduate studies. He received Master of Science degree in Polymer Engineering in March, 1988. He continued for a doctorate degree and received Doctor of Philosophy degree in Polymer Engineering in June of 1991.

He is a member of Phi Kappa Phi honor society and society of Plastics Engineers. He will join Dow Chemicals in Freeport, Texas, after graduation.