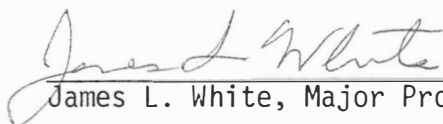
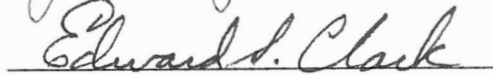
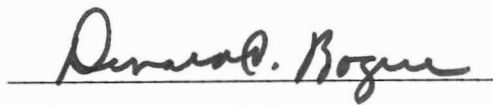
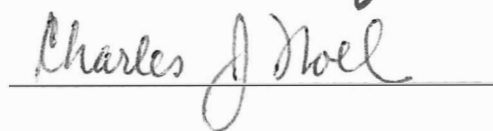


To the Graduate Council:

I am submitting herewith a dissertation written by Vilas G. Bankar entitled "Rheology, Dynamics and Structure Development During Melt Spinning of Nylon-6." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.


James L. White, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted to the Council:


Vice Chancellor
Graduate Studies and Research

Thesis
766
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RHEOLOGY, DYNAMICS AND STRUCTURE DEVELOPMENT DURING
MELT SPINNING OF NYLON-6

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

Vilas G. Bankar

March 1976

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ABSTRACT

A comprehensive study of melt spinning dynamics and structure development of nylon-6 was performed. The major emphasis of the research consisted of on-line rheological and morphological measurements. These included diameter, temperature and tension measurements of the fiber as well as x-ray diffraction and birefringence measurements. The effects of annealing spun fibers in air, water and 20 percent formic acid solution were also studied. Tensile properties of spun fibers were measured and related to the spinning variables and structural characteristics.

In the rheological portion of the work, the shear viscosity and the normal stresses in nylon-6 melts were measured. Nylon-6 melt shows more Newtonian-like behavior in shear experiments than does polyethylene and shows very low normal stresses. Rheological response in melt spinning was interpreted in terms of an elongational viscosity. In the spinline, nylon-6 behaves more like a viscoelastic fluid with the ratio of elongational viscosity to shear viscosity being about 15.

In studies of the dynamics of melt spinning various force components in the spinline were calculated. The gravity force was negligible at high take-up speed but was significant at low speed. The inertia and the aerodynamic drag showed an opposite behavior. The rheological force decreased along the spinline at low take-up speeds, remained constant at intermediate speeds and increased at higher speeds.

In the structure development studies, on-line x-ray patterns of

nylon-6 exhibited an amorphous halo. This was true whether spinning was done in 65 percent or 100 percent relative humidity. Nylon-6 crystallized in a γ -pseudohexagonal form on the bobbin in the presence of moisture. The small angle x-ray scattering from conditioned fibers showed a diffuse ring at low take-up speeds but a two point diagram for fiber spun at high take-up speeds.

Nylon-6 changed slowly from a γ -pseudohexagonal structure into an α -monoclinic structure when annealed at increasingly higher temperature. The rate of change was greatest when annealed in formic acid, but lowest in air, while intermediate in water.

The tensile strength and the modulus of spun fibers increased but the elongation to break decreased with increasing take-up speed or spinline stress. Similar behavior was observed when the properties were correlated with the birefringence and the c-axis orientation factor.

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CHAPTER I

INTRODUCTION

Since the beginning of civilization, cloth has been one of the basic needs of human beings. Before synthetic fibers were invented, man had to depend on naturally occurring fibers such as cotton, wool and silk for his clothing needs. The everlasting quest of man to compete with nature and simulate natural things has led to the development of man-made fibers which, in some instances, surpass natural fibers, especially silk, in properties and strength.

In 1842, a British silk weaver, Louis Schwabe exhibited a machine for making artificial filaments and in 1845, Richard Brooman obtained a patent for extruding gutta-percha thread which was taken up under tension on a roll (25). The development of man-made fibers really began in 1884 when Count Hilaire de Chardonnet of France made fibers by extruding strands of nitro cellulose dissolved in a solution of alcohol and ether (114). The first commercial production of cellulose nitrate fibers began in 1891 in France. This fiber became known as Chardonnet silk.

This fiber was made by solution spinning. Many important fibers of today, such as nylon, polyester, and polypropylene are made by melt spinning wherein a polymer is melted in a reservoir and extruded through small holes. The molten filament is solidified by cooling and is taken up on a bobbin.

The first attempt to produce a fiber from melt was reported by

Carothers and Hill of E. I. duPont de Nemours in 1932 (30). Their efforts led to the development of nylon fibers. A history of development of nylon fibers has been given by Bolton (21), the then Chemical Director of duPont. Nylon was first commercialized in 1939 by duPont.

There were no published efforts made to understand the melt spinning process until the late 1950's. In 1959, Ziabicki and Kedzierska, both working with a Polish fiber industry, began publishing a series of papers describing theoretical and experimental work on melt spinning of fibers. Since then many scientists and engineers have undertaken a study of melt spinning.

Numerous papers have been published in the technical literature concerning the relationship of spinning conditions to fiber quality and properties.

The purpose of this dissertation was to study both rheology and structure development during melt spinning of nylon 6. The rheological response in both isothermal and non-isothermal spinning was studied by direct examination of the spinline and the measurement of diameter, tension, and temperature of the spinline. The experimental results have been compared with the theoretical predictions using different rheological models for the spinline. The structure development has been studied by making x-ray diffraction patterns and birefringence measurements on the running spinline. The morphology of spun fibers has also been studied and related to the spinning conditions and mechanical properties.

CHAPTER II

LITERATURE SURVEY

A. NYLON-6

General

Nylons belong to a general class of polyamides which are condensation products which contain recurring amide groups NH-CO as integral parts of the main polymer chains. The term "nylon" is defined as "a generic term for any long chain synthetic polyamide which has recurring amide groups as an integral part of the main polymer chain, and which is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis" (122).

Nylons were first synthesized by Wallace H. Carothers and Julian Hill when they were trying to find a polymer which could be used as a synthetic fiber. This fundamental research was carried out in the E. I. duPont de Nemours Company. Nylons soon became important commercial fibers because of their remarkable strength, resistance to abrasion and durability.

There are different types of nylons. They are distinguished from each other by a system of nomenclature which depends upon the number of carbon atoms in the starting materials used for making nylons. This nomenclature has been given in the literature (93). The most commercially important nylons are nylon-6, made from caprolactam, and nylon 66, made from hexamethylene diamine and adipic acid.

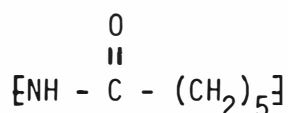
A stabilizer such as acetic acid is added to caprolactam to control the molecular weight. A mixture of molten caprolactam, water and acetic acid is fed to a heated polymerization column called a VK tube. The temperature is maintained between 250°C and 270°C and the residence time is about 24 hours. The polycaprolactam is extruded from the bottom of the tube, quenched in water and cut into small pellets. These pellets contain an equilibrium amount of about 10 percent monomer and other oligomers. These are removed by washing the pellets with boiling water. They are then dried to less than 0.1 percent moisture content before spinning.

Properties

Nylon-6 melts at 215-220°C depending on its molecular weight. It is soluble in some acids and organic solvents. It is quite stable in alkaline solutions, but decomposes in acidic solutions. Nylon-6 is chemically unaffected by water at ordinary temperatures, but at high temperatures, in the presence of moisture, hydrolysis and degradation occurs.

Structural Characteristics and General Morphological Features

Nylon-6 molecule is practically linear with the chemical repeat unit



When these chains come close to each other during crystallization, there is a possibility of forming hydrogen bonds between the carbonyl

groups of one chain and the amine groups of the other. Such hydrogen bonds are indeed formed, as it is evident from the measurement of inter-chain distance ($4.8\text{\AA}$) which is typical of a hydrogen bond; and also from infrared studies (112).

The study of crystal structure of nylon-6 was first carried out by Brill (24) and later by Holmes, Bunn and Smith (74). The latter authors made extensive studies of drawn nylon-6 fibers and determined the symmetry of the unit cell, its dimensions, and the atomic coordinates. The unit cell of nylon-6 proposed by these authors is monoclinic with dimensions

$$a = 9.56\text{\AA}$$

$$b = 17.24\text{\AA} \quad \text{angle } \beta = 67.5^\circ$$

$$c = 8.01\text{\AA}$$

From the measurement of repeat distance along the chains and of C-C bond length, they concluded that the chains of drawn nylon-6 are extended planar zig-zag. The b-axis of a monoclinic unit cell is considered to be the axis of symmetry by convention. For nylon-6, this is also the chain axis ($b = 17.24\text{\AA}$).

Hydrogen bonding between the amide and the carbonyl groups of adjacent nylon-6 chains results in the formation of hydrogen bonded sheets. The adjacent chains in these sheets are strictly antiparallel. This makes perfect hydrogen bonds. In the monoclinic form, a nylon-6 crystal is formed by stacking these sheets together. The sheets are staggered up and down. A schematic diagram of the hydrogen bonded sheets

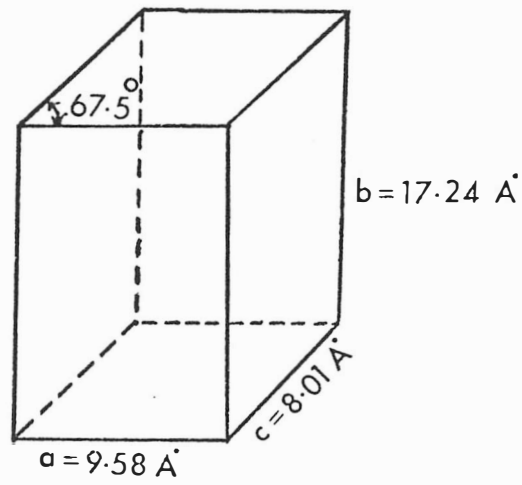
as well as their staggered arrangement is shown in Figure II-1. Also shown is a drawing of the nylon-6 unit cell.

Holmes, Bunn and Smith also noted the existence of another crystalline form of nylon-6 which produced x-ray patterns obviously different from x-ray patterns of monoclinic nylon-6. This crystalline form was less stable and it was difficult to isolate it. It always existed along with the monoclinic form. This form, later known as pseudo-hexagonal or γ -form, was also studied by Kinoshita (91), Arimoto (7) and Vogelsong (169). These authors (7, 91, 169) and others (164, 23, 113) obtained the γ -form by treatment of ordinary monoclinic form (α -form with an aqueous solution of iodine-potassium iodide and then removing iodine by washing with aqueous sodium-thiosulphate. Ziabicki (189) reported that a pseudo-hexagonal form can also be obtained by melt spinning nylon-6. Ziabicki has discussed the conversion of this phase to the normal monoclinic phase (187). There is a marked difference in the x-ray patterns of these two major crystalline forms of nylon-6, α (monoclinic) and γ (pseudo-hexagonal) (74, 132, 23, 113). The γ -form whose x-ray pattern is shown in Figure II-2 is apparently the same as the β -form described by Holmes, et al. (74). The most obvious differences in the two patterns are:

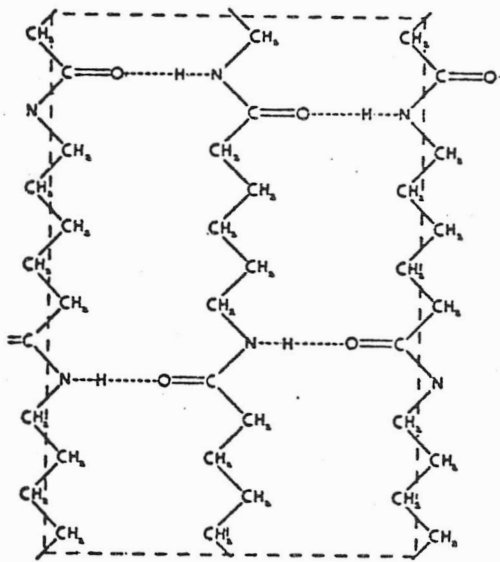
(1) The presence of two equatorial peaks ($4.4\text{\AA}$ and $3.6\text{\AA}$) in the α -pattern against only a single peak ($4.2\text{\AA}$) in the γ -pattern.

(2) Presence of strong meridional peak ($8.2\text{\AA}$) in the γ -form. This is very weak or sometimes absent in the α -form.

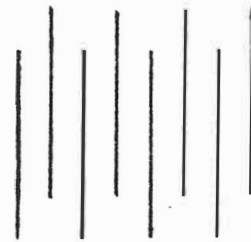
The unit cell dimensions of the γ -pseudo-hexagonal crystal structure as reported by Vogelsong (169) are



(A) Unit Cell

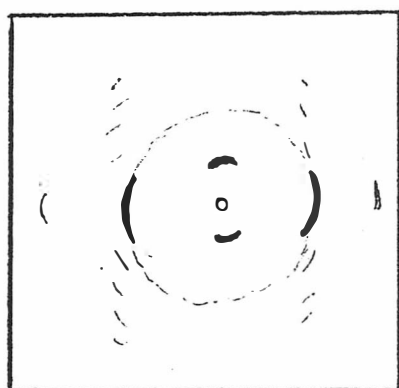


(B) Hydrogen Bonded Sheet

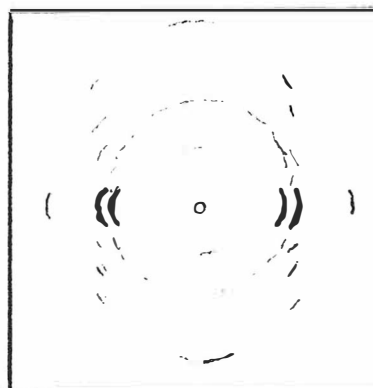


(C) Staggering of Hydrogen Bonded Sheets

Figure II-1. Schematic of monoclinic crystal structure of nylon-6.



(A) γ -Pseudohexagonal



(B) α -Monoclinic

Figure II-2. Wide angle x-ray diffraction patterns of two crystalline forms of nylon-6.

$$a = b = 4.79\text{\AA}$$

$$c = 16.70 \quad \text{angle } \gamma = 60^\circ$$

According to Arimoto (7) the γ -form is actually monoclinic with $a = 9.33\text{\AA}$, $b = 16.88\text{\AA}$, $c = 4.78\text{\AA}$ and $\beta = 121^\circ$.

Besides these two major crystal structures of nylon-6, Roldan and Kaufman (132) have reported several other forms including amorphous, β (hexagonal) and α -paracrystalline (monoclinic) forms.

Single crystals of nylon-6 have been obtained by Geil (60) by precipitating nylon-6 from glycerin solution. The thickness of these single crystal lamellae was about $60\text{\AA}$. Ogawa, et al. (123) pointed out that the diffraction pattern of nylon-6 single crystals corresponds to the γ -pseudo-hexagonal form. Geil (60) also observed that spherulites were formed along with single crystals in the same solution.

Spherulitic structure was also observed in melt-crystallized nylon-6 by Magill (101) and Inoue (78). The diameters of spherulites varied between $10\text{--}50\mu$ depending on the temperature of crystallization.

Crystallization Kinetics

The crystallization kinetics of nylon-6 have been studied by a few authors. Burnett and McDevit (27) obtained a growth rate of nylon-6 spherulites at temperatures ranging from 102°C to 182°C using an optical microscope and a motion picture camera. A typical bell-shaped curve was obtained when the rate of growth was plotted against temperature. At constant temperature the growth rate was found to be constant. Inoue (77) obtained crystallization isotherms of nylon-6 at temperatures

ranging from 205 to 215°C using a dilatometric technique. The Avrami equation was used to calculate the half-times of crystallization, $t_{1/2}$. The half-time was found to be 18 minutes or higher depending on the crystallization temperature. The rate of crystallization was found to be lower for polymers of higher molecular weight. In a later paper (78) he studied the effects of various nucleating agents on the rates of crystallization. The use of nucleating agents resulted in decrease of induction time and increase of crystallization rates.

Magill (100) studied the effects of melt history, moisture content and relative viscosity on induction time during isothermal crystallization. He also measured the kinetics of isothermal crystallization over a wide range of temperature using a cine camera technique and depolarized light intensity (101). The maximum rate of crystallization was found to occur at about 140°C. The half-time of crystallization was ten seconds for a crystallization temperature of 140°C and higher at higher crystallization temperatures. No papers have appeared on the kinetics of strain induced crystallization of nylon-6.

Effect of Moisture

Moisture plays an important role during polymerization of nylon-6 from caprolactam. It acts as an initiator during polymerization as shown in Equation II-1. Depolymerization of nylon-6 also takes place when it is heated in the presence of water. The polycondensation equilibrium shown below is established between the amide groups and water molecules.



Smith (144) has shown that the equilibrium concentration of $-\text{NH}_2$ and $-\text{COOH}$ end groups increased when nylon-6 is heated at 250°C with increasing amount of water.

The effects of moisture on the physical properties of nylons at ordinary temperatures have been known for a long time. When kept in humid atmosphere, nylon-6 absorbs moisture. The equilibrium moisture content reaches as high as 9 percent at 100 percent R. H. (156). The elastic modulus and yield stress of nylon-6 decrease with increasing moisture content (143). Moisture acts as a plasticizer and generally reduces the strength of nylon-6.

Miyasaka and Ishikawa (113) studied the effect of moisture on the crystalline transition of nylon-6. The transition was achieved by drawing. It was observed that at very low temperatures, such as -75°C , the transition was more effective when the sample was dry. However, at 60°C , the transition was more effective for wet samples.

Campbell (29) has studied the effect of water on the x-ray diffractometer scans of nylon-6 films crystallized in α -form. Water caused changes in the amorphous as well as the crystalline regions. It was found that the intensity of the combined (002) and (202) peaks decreased and that of (200) peak increased on water absorption.

B. RHEOLOGY

Constitutive Equations

One of the major goals of the study of rheology is the development

of models generally called constitutive equations which relate stresses in a material to deformations. These models have to be formulated in such a way as to explain the experimentally observed behavior of the material. Many of the early analyses of polymer processing operations are based upon the constitutive equations of Newtonian fluids, or simple one dimensional power-law fluids. They do not explain many of the phenomena observed such as normal stresses, stress relaxation, etc.

The theories of constitutive equations for viscoelastic fluids which polymer melts are generally considered to be, are classified broadly into two basic groups as differential and integral theories.

Differential Theories. Differential theories originate from Maxwell's equation (104)

$$P + \tau \frac{dP}{dt} = G\tau \frac{d\gamma}{dt} \quad , \quad G\tau = \eta \quad (\text{II-5})$$

where P is the stress, τ is the relaxation time, γ is the deformation, G is the elastic modulus and η is the viscosity.

Maxwell's equation is a linear one dimensional theory and predicts neither non-Newtonian viscosity nor normal stresses. It was generalized to a three dimensional form by Zaremba (185) in 1903. Zaremba's theory is well able to explain non-Newtonian viscosity and normal stresses. Noll (121) and White and Metzner (174) have proposed other forms of non-linear Maxwell models. Oldroyd (132, 126), Williams and Bird (178), Spriggs and Bird (150, 151) among others have developed similar models which involve higher order derivatives of γ .

The White-Metzner equation can be written in three dimensional form as

$$\underline{g} = -p\underline{I} + \underline{P} \quad (\text{II-6a})$$

$$\underline{P} + \tau \frac{\delta \underline{P}}{\delta t} = 2G\tau \underline{d} \quad (\text{II-6b})$$

where

$$\frac{\delta P_{ij}}{\delta t} = \frac{\partial P_{ij}}{\partial t} + V_m \frac{\partial P_{ij}}{\partial x_m} - \frac{\partial V_i}{\partial x_j} P_{mj} - \frac{\partial V_j}{\partial x_m} P_{im} \quad (\text{II-6c})$$

p = pressure, V = velocity, $\underline{d}$ = rate of deformation tensor, $\underline{g}$ = stress tensor and $\underline{I}$ = unit tensor.

This equation gives reasonable agreement with laminar shear flow viscosity and normal stress experiments if the relaxation time is taken to be a function of deformation rate.

In general the usefulness of rate theory is limited by (1) its inability to quantitatively represent stress relaxation and dynamic sinusoidal oscillation data and (2) the necessity of solving six simultaneous complex differential equations for the stress component in all but the simplest flows.

Integral Theories. Integral theories are based upon Boltzmann's superposition principle (22). Boltzmann's constitutive equation utilizes a memory function which is decreasing with time. Boltzmann's equation can be written in a three dimensional form as:

$$g(t) = -pI + 2 \int_{-\infty}^t G(t-s) d(s) ds \quad (II-7)$$

where

t is the current time.

s is the past time.

$G(t-s)$ is the memory function which is decreasing with $(t-s)$.

Equation II-7 may be written in an alternate form after integrating by parts.

$$\sigma(t) = -pI + 2 \int_{-\infty}^t \phi(t-s) \varepsilon(s) ds \quad (II-8)$$

where

$$\phi(t) = -dG(t)/dt$$

and $\varepsilon(s)$ is the infinitesimal strain tensor.

In terms of relaxation spectrum, $\phi(t)$ can be written as

$$\phi(t) = \int_{-\infty}^{+\infty} \frac{H(\tau)}{\tau} e^{-t/\tau} d \ln \tau \quad (II-9)$$

where $H(\tau)$ is the spectrum of relaxation times.

It may be shown that the Maxwell equation is a special case of Boltzmann equation for which $G(t) = G_0 e^{-t/\tau}$ and $\phi(t) = \frac{G_0}{\tau} e^{-t/\tau}$.

The Boltzmann equation is valid for infinitesimal strains. In practice, deformation rates are very large. The first attempts to generalize Boltzmann's theory to large deformations were made by Oldroyd (124) and Lodge (99) and subsequent further development to a very

general non-linear model was given by Green and Rivlin (63) who assumed that stress is an hereditary functional of the deformation history. Coleman and Noll (43) later gave more elegant formulations of Green-Rivlin concepts. The arbitrary functional in this theory may be expanded in the Frechet functional polynomials. The stress tensor may then be written as

$$\begin{aligned} \sigma_{ij} = & -p\delta_{ij} + \int_{-\infty}^t \phi(t-s) e_{ij}(s) ds \\ & + \int_{-\infty}^t \int_{-\infty}^t \psi(t-s_1, t-s_2) e_{im}(s_1) e_{mj}(s_2) ds_1 ds_2 + \dots \end{aligned} \quad (\text{II-10})$$

where $\phi(s)$, $\psi(s_1, s_2)$, etc. are relaxation functions and e_{ij} is the component of large strain tensors. Two such possible tensors are that of Finger tensor, c_{ij}^{-1} , and Cauchy tensor c_{ij}

$$c_{ij}^{-1} = \frac{\partial x_i}{\partial \bar{x}_a} \cdot \frac{\partial x_j}{\partial \bar{x}_a} \quad c_{ij} = \frac{\partial \bar{x}_a}{\partial x_i} \cdot \frac{\partial \bar{x}_a}{\partial x_j} \quad (\text{II-11})$$

x 's and $\bar{x}$'s being the present and the past configurations at time t and time s respectively.

For smooth flows it is possible to express the strain tensors $e_{ij}(s)$ in Equation II-10 in terms of Rivlin-Erickson acceleration tensors $B_{ij}^{(n)}$ by expanding it in Taylor's series in time about its instantaneous state.

$$e_{\sim}(s) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1} (t-s)^n}{2n!} B_{\sim n}(t) \quad (\text{II-12})$$

where

$$B_{ij}^{(1)} = 2d_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \quad (\text{II-12a})$$

$$B_{ij}^{(n+1)} = \frac{D}{Dt} B_{ij}^{(n)} - \sum_m \frac{\partial v_i}{\partial x_m} B_{mj}^{(n)} - \sum_m \frac{\partial v_j}{\partial x_m} B_{im}^{(n)} \quad (\text{II-12b})$$

Equation II-10 may now be written as

$$g_{\sim} = -p_{\sim} I + \sum_{n=1}^{\infty} M_{\sim n} \quad (\text{II-13})$$

where

$$M_{\sim 1} = \omega_1 B_{\sim 1} \quad (\text{II-13a})$$

$$M_{\sim 2} = \omega_2 B_{\sim 1}^2 + \omega_3 B_{\sim 2} \quad (\text{II-13b})$$

$$M_{\sim 3} = \omega_4 [\text{tr } B_{\sim 1}^2] B_{\sim 1} + \omega_5 [B_{\sim 1} B_{\sim 2} + B_{\sim 2} B_{\sim 1}] + \omega_6 B_{\sim 3} \quad (\text{II-13c})$$

The coefficients ω_j are the integrals of the relaxation moduli.

The term of first order in $M_{\sim n}$ is identical to the Newtonian fluid; whereas including second and third order terms in the constitutive equation would yield so called second order and third order fluid.

$$\underline{\sigma} = -p\underline{I} + \underline{M}_1 = -p\underline{I} + \omega_1 \underline{B}_1 \quad \text{Newtonian fluid} \quad (\text{II-14})$$

$$\underline{\sigma} = -p\underline{I} + \omega_1 \underline{B}_1 + \omega_2 \underline{B}_1^2 + \omega_3 \underline{B}_2 \quad \text{Second order fluid} \quad (\text{II-15})$$

$$\begin{aligned} \underline{\sigma} = & -p\underline{I} + \omega_1 \underline{B}_1 + \omega_2 \underline{B}_1^2 + \omega_3 \underline{B}_2 + \omega_4 [\text{tr } \underline{B}_1^2] \underline{B}_1 \\ & + \omega_5 [\underline{B}_1 \underline{B}_2 + \underline{B}_2 \underline{B}_1] + \omega_6 \underline{B}_3 \quad \text{Third order fluid} \quad (\text{II-16}) \end{aligned}$$

Although very general, the Green-Rivlin constitutive equation containing multiple integrals is very complex. In 1963, Bernstein, Kearsley and Zapas (BKZ) (16) proposed a constitutive equation containing single integral. Later in 1965, Zapas and Craft (184) showed on the basis of multiple step stress relaxation experiments that such a single integral expression was sufficient to describe the stress-strain behavior of polyisobutylene. The BKZ results could be written after simplification as

$$\begin{aligned} \underline{\sigma} = & -p\underline{I} + \int_0^t [m_1(t-s, I_{\underline{\zeta}}^{-1}, II_{\underline{\zeta}}^{-1}) \underline{\zeta}^{-1} \\ & - m_2(t-s, I_{\underline{\zeta}}^{-1}, II_{\underline{\zeta}}^{-1}) \underline{\zeta}] ds \quad (\text{II-17}) \end{aligned}$$

where

$$I_{\underline{\zeta}}^{-1} = \text{tr } \underline{\zeta}^{-1} \quad \text{and} \quad II_{\underline{\zeta}}^{-1} = \text{tr}(\underline{\zeta}^{-1})^2$$

m_1 and m_2 are the relaxation functions.

Other versions of the single integral model were developed by Bird and Carreau (18) and Bogue (20) which was later modified by White, Bird and Carreau expressed the constitutive equation in terms of Cauchy's and Finger's strain tensors and the relaxation moduli as function of second invariant of the deformation rate. Bogue utilized time averaged integrals of rate of deformation invariants over the history of the deformation. The Bogue-White model can be written as

$$\underline{\underline{g}} = -p\underline{\underline{I}} + \int_{-\infty}^t [m_1(t-s, \overline{II}_d) \underline{\underline{C}}^{-1} - m_2(t-s, \overline{II}_d) \underline{\underline{C}}] ds \quad (II-18)$$

$$m_1(t-s, \overline{II}_d) = (1 + \frac{\epsilon}{2})^\Sigma \frac{G_i}{\tau_{eff}(i)} e^{-(t-s)/\tau_{eff}(i)} \quad (II-18a)$$

$$m_2(t-s, \overline{II}_d) = \frac{-\epsilon/2}{1 + \epsilon/2} m_1(t-s, \overline{II}_d) \quad (II-18b)$$

$$\tau_{eff}(i)^{-1} = \tau_i^{-1} + a \overline{II}_d^{1/2} \quad (II-18c)$$

$$\overline{II}_d^{1/2} = \frac{1}{(t-s)} \int_0^{(t-s)} \overline{II}_d^{1/2} dz \quad (II-18d)$$

Here "a" is a constant coefficient and ϵ is a dimensionless parameter describing deviations from Weissenberg hypothesis. In terms of a continuous deformation, Bogue-White model is written as

$$m_1(t - s, \overline{II}_d) = (1 + \frac{\epsilon}{2}) \int_0^{\tau_{eff}^m} \frac{H(\frac{\tau'}{1 - a\tau' \overline{II}_d^{1/2}})}{1 - a\tau' \overline{II}_d^{1/2}} \frac{e^{-\frac{(t-s)}{\tau'}}}{\tau'^2} d\tau' \quad (II-18e)$$

The Bogue-White model was used by Chen and Bogue (37) in predicting shear and normal stresses in polyethylene and polystyrene. Middleman (109) and Furuta, Lobe and White (58) use it to predict transient stress build up in elastomers.

A simpler form of the Bogue-White model can be used for moderately narrow molecular weight distribution polymers whose complete relaxation spectra, $H(\tau)$, are not readily available. For such moderately narrow molecular weight distribution polymers, Tobolsky (160) and Ninomiya and Fujita (119) have shown that the relaxation spectrum has a "wedge-box" type of distribution. When the complete relaxation spectrum is not available the "box" distribution $H(\tau) = H_0$ becomes particularly useful. With this simplification, the complete Bogue-White model is

$$\dot{\gamma} = -p\dot{\gamma} + \int_{-\infty}^t [m_1(t - s, \overline{II}_d) \dot{\gamma}^{-1} - m_2(t - s, \overline{II}_d) \dot{\gamma}] ds \quad (II-19)$$

$$m_1(t - s, \overline{II}_d) = (1 + \frac{\epsilon}{2}) \int_0^{\tau_{eff}^m} \frac{H_0}{1 - a\tau' \overline{II}_d^{1/2}} \frac{e^{-(t-s)/\tau'}}{\tau'^2} d\tau' \quad (II-19a)$$

$$m_2(t - s, \overline{II}_d) = -\frac{\epsilon/2}{1 + \frac{\epsilon}{2}} m_1(t - s, \overline{II}_d) \quad (II-19b)$$

$$\tau_{\text{eff}}^m = \frac{\tau_m}{1 + a\tau_m \text{II}_d^{1/2}} \quad (\text{II-19c})$$

$$\overline{\text{II}_d^{1/2}} = \frac{1}{(t-s)} \int_0^{(t-s)} \text{II}_d^{1/2} dz \quad (\text{II-19d})$$

Elongational Flow

Experimental. The earliest experiments on elongational flow behavior are by Trouton who first introduced the concept of elongational viscosity (163). He studied extension of pitch, tar and wax and defined elongational viscosity as

$$\chi = \frac{\sigma_{11}}{dv/dx} = \frac{\text{elongational stress}}{\text{elongation rate}} \quad (\text{II-20})$$

He showed that it was three times the shear viscosity.

In recent years several papers were published concerning measurements of elongational viscosity. Transient increase of stresses in samples subjected to constant elongation rate was observed by Ballman (13), Meissner (105), Vinogradov, et al. (168) and Stevenson (155). Ballman observed that the stresses in polystyrene samples build up slowly to a steady state. The steady state elongational viscosity was found to be approximately constant, independent of elongational rate. Meissner (105) observed that the stresses in low density polyethylene reached steady state for only low elongation rates whereas at high rates they increase continuously without limit.

Vinogradov, et al. (168) conducted similar experiments on

polyisobutylene and observed that the elongational viscosity passes through a maximum before attaining a steady state.

Stevenson (155) reported that the elongational viscosity of isobutylene-isoprene co-polymer reached a steady state value at all the elongation rates investigated (10^{-4} - 10^{-1} sec $^{-1}$). The steady state value was equal to three times the shear viscosity. However, no steady state was obtained in case of cis-1, 4 polyisoprene. Cogswell (40, 41, 42) also carried out constant elongation rate experiments along with constant stress experiments and convergent flow analysis. However, some of these experiments are crude and give only approximate results. His results show that the elongational viscosity increases with elongation stress for low density polyethylene, decreases for polypropylene whereas remains constant for polymethylmethacrylate.

Chen and co-workers (38) and Takaki and Bogue (158) have made extensional studies in falling weight type of experiments where a polymer rod was stretched isothermally using a constant force. The results were analyzed using non-linear viscoelastic model of Bogue-White. A good agreement was obtained between the predicted and the experimental stress-time curves.

There have been many measurements of extensional properties in a melt spinning type of geometry (188, 84, 85, 81, 2, 38, 96). They will be discussed later in the section on melt spinning.

Theoretical. The elongational flow of polymer fluids was first studied by Nitschmann and Schrade (120) who suggest that λ increases with elongational rate. Yamamoto (180) determined elongational viscosity-

elongation rate for network structures. At high rate of entanglement breakage, χ was finite and showed a maximum. At low breakage rate, χ went to infinity at finite elongation rate.

Coleman and Noll (44) discussed the application of the simple fluid theory to steady elongation of an incompressible cylindrical rod. White (172) and Markovitz and Coleman (102) used the second order theory of simple fluids and showed that the elongational viscosity increases with elongation rate. The same effect was observed by Roscoe (133) who applied the third order simple fluid theory to simple elongation.

Lodge (98) applied his single-integral fluid model to simple elongation and showed that for low elongation rates, χ is equal to 3η where η is the shear viscosity. It grows without bound as the elongation rate approaches a critical value. Lodge's result is a special case of Yamamoto's.

Other single integral models which give unbounded viscosity at finite elongation rate include those of Bird and Carreau (18) and Meister (106).

Adams (3) used Bernstein-Kearsley-Zapas model (16) and showed that χ goes through a slight maximum and then decreases as E increases. Casey (33), using Bogue model showed that χ increases with E .

Denn and Marrucci (50) applied the White-Metzner model to uniaxial stretching to obtain the transient stress response. For small elongation rates, the response is linear viscoelastic but above a critical value, the stresses grow indefinitely. They conclude on a basis of simple theoretical analysis and some experimental evidence that the existence of a critical elongation rate is an artifact of the models which predict it.

The unbounded value of λ or stresses may never be obtained in a steady state sense, i.e., the stresses "blow up" before the steady state is achieved.

Chang and Lodge (34), using Lodge's model obtained a qualitative agreement with the transient data of Meissner (105).

A review of early research on extensional flow of non-Newtonian fluids is given by Dealy (47).

Application of Constitutive Equations to Simple Shear and Uniaxial

Elongation

It is interesting to look at the response of rheological models discussed in the previous section to a flow field of simple shear and uniaxial elongation.

The kinematics for a simple shear flow are described as

$$v_1 = \dot{\gamma}x_2 \quad v_2 = v_3 = 0 \quad (\text{II-21})$$

where $\dot{\gamma}$ is the rate of shear, dv_1/dx_2 . Subscripts 1 and 2 indicate the directions of flow and shear respectively. The relationships between the material co-ordinates at the time t and s can be written as

$$x_1(t) = \bar{x}_1(s) + \dot{\gamma}x_2(t - s) = \bar{x}_1(s) + \dot{\gamma}x_2z$$

$$x_2(t) = \bar{x}_2(s)$$

$$x_3(t) = \bar{x}_3(s) \quad (\text{II-22})$$

For uniaxial elongation, the kinematics are written as

$$v_1 = \dot{E}x_1 \quad v_2 = -\frac{\dot{E}}{2}x_2 \quad v_3 = -\frac{\dot{E}}{2}x_3 \quad (\text{II-23})$$

where $\dot{E}$ is the constant elongation rate.

The material co-ordinates may be written as

$$\begin{aligned} x_1(t) &= \bar{x}_1(s) \exp [\dot{E}(t - s)] \\ x_2(t) &= \bar{x}_2(s) \exp \left[-\frac{\dot{E}}{2}(t - s)\right] \\ x_3(t) &= \bar{x}_3(s) \exp \left[-\frac{\dot{E}}{2}(t - s)\right] \end{aligned} \quad (\text{II-24})$$

Equations II-22 and II-24 can be used to obtain various strain tensors appearing in the constitutive equations and the material parameters like the shear viscosity, the first normal stress difference coefficient, and the elongational viscosity can be evaluated. The response of some of the rheological models is shown in Table 1.

Rheological Properties and Their Measurements

In order to use the constitutive equation to describe the fluid behavior we need to know the rheological properties of the material. These are usually measured in the simple geometries such as capillary tubes or rotating discs or cones. The flows in such geometries are sometimes called viscometric flows or simple laminar shear flows.

TABLE 1
RESPONSE OF RHEOLOGICAL MODELS TO SIMPLE SHEAR AND ELONGATION

Model	Shear Viscosity η	First Normal Stress Difference Coefficient ψ_1	Elongational Viscosity χ
Newtonian Fluid Equation II-14	$\eta = \omega_1$	$\psi_1 = 0$	$\chi = 3\omega_1$
Second Order Fluid Equation II-15	$\eta = \omega_1$	$\psi_1 = -2\omega_3$	$\chi = 3\omega_1 \left[1 + \frac{\omega_2 - \omega_3}{\omega_1} \dot{\epsilon} \right]$
Third Order Fluid Equation II-16	$\eta = \omega_1 + 2(\omega_4 - \omega_5) \dot{\gamma}^2$	$\psi_1 = -2\omega_3$	$\chi = 3\omega_1 \left[1 + \frac{\omega_2 - \omega_3}{\omega_1} \dot{\epsilon} + \frac{6(\omega_4 - \omega_5) + 3\omega_6}{\omega_1} \dot{\epsilon}^2 \right]$
White-Metzner Fluid Equation II-6	$\eta = G\tau_{eff}$	$\psi_1 = 2G\tau_{eff}^2$	$\chi = \frac{3G\tau_{eff}}{(1 + \dot{\epsilon}\tau_{eff})(1 - 2\dot{\epsilon}\tau_{eff})}$
Bogue-White Model Equation II-19	$\eta = H_0 \tau_m \left[\frac{\ln(1 + \frac{a\tau_m \dot{\gamma}}{\sqrt{2}})}{(\frac{a\tau_m \dot{\gamma}}{\sqrt{2}})^2} \right]$	$\psi_1 = 2H_0 \tau_m^2 \left[\frac{\ln(1 + \frac{a\tau_m \dot{\gamma}}{\sqrt{2}})}{(\frac{a\tau_m \dot{\gamma}}{\sqrt{2}})^2} - \frac{1}{\frac{a\tau_m \dot{\gamma}}{\sqrt{2}} (1 + \frac{a\tau_m \dot{\gamma}}{\sqrt{2}})} \right]$	$\chi^* = \frac{3H_0}{\dot{\epsilon}} \left[\frac{a' \ln(1 + a' \dot{\epsilon}\tau_m)}{(1 + a')(a' - 2)} + \frac{1}{3(1 + a')} \ln\left(1 + \frac{\dot{\epsilon}\tau_m}{1 + a' \dot{\epsilon}\tau_m}\right) + \frac{2}{3(a' - 2)} \ln\left(1 - \frac{2\dot{\epsilon}\tau_m}{(1 + a' \dot{\epsilon}\tau_m)}\right) \right]$ $a' = \sqrt{\frac{3}{2}} a$

* ϵ in Equation II-19 is assumed to be zero in deriving this equation.

The stress tensor in a laminar shear flow of a viscoelastic fluid may be written as (19)

$$\underline{g} = -p\underline{I} + \underline{P} \quad (\text{II-25})$$

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{pmatrix} = \begin{pmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{pmatrix} + \begin{pmatrix} \beta_1 \dot{\gamma}^2 & \eta \dot{\gamma} & 0 \\ \eta \dot{\gamma} & \beta_2 \dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (\text{II-26})$$

Thus the viscometric flow field can be completely described by three stresses; the shear stress and the two normal stresses and we need to determine three material functions.

$$\eta(\dot{\gamma}) = \sigma_{12} / \dot{\gamma} \quad \text{shear viscosity} \quad (\text{II-27})$$

$$\begin{aligned} \psi_1(\dot{\gamma}) &= (\sigma_{11} - \sigma_{22}) / \dot{\gamma}^2 && \text{first normal stress} \\ &= \beta_1 - \beta_2 && \text{difference coefficient} \end{aligned} \quad (\text{II-28})$$

$$\begin{aligned} \psi_2(\dot{\gamma}) &= (\sigma_{11} - \sigma_{33}) / \dot{\gamma}^2 && \text{second normal stress} \\ &= \beta_2 && \text{difference coefficient} \end{aligned} \quad (\text{II-29})$$

The viscosity function and its dependence on shear rate has been widely studied for polymer solutions and melts in a variety of viscometers by numerous investigators. The viscosity is found to have a constant value at low shear rates; but drops rapidly as the shear rate is

increased. The existence of normal stresses was first shown by Weissenberg in 1948 (170).

The first normal stress difference was experimentally found to be positive, first by Freeman and Weissenberg (56) and later by Pollet and Cross (130). Weissenberg suggested that the second normal stress difference was zero in viscometric flow. This became popular as Weissenberg's hypothesis. However, in recent years the second normal stress difference has generally been found to be negative and of the order of one-tenth of the first normal stress difference (61, 62, 159, 111). Two most widely used rheometers for measuring viscosity and normal stresses are described below.

Cone-and-Plate Viscometer. The cone-and-plate viscometer, also known as the Weissenberg rheogoniometer has been widely used for measurement of normal stresses in polymer solutions and melts. In this geometry, the polymer fluid is sheared between a rotating cone and a stationary plate. The torque required to keep the plate stationary and the force F pushing apart the cone and the plate are measured and related to the shear stress and the first normal stress difference through the expressions (56, 45, 110)

$$T = \int_0^R 2\pi r^2 \sigma_{12} dr = \frac{2}{3} \pi R^3 \sigma_{12} \quad (\text{II-30})$$

$$N_1 = 2F/\pi R^2 \quad (\text{II-31})$$

The shear rate is given by

$$\dot{\gamma} = \frac{\Omega}{\psi} \quad (\text{II-32})$$

The viscosity is given by

$$\eta = \frac{\sigma_{12}}{\dot{\gamma}} = \frac{3T}{2\pi R^3} \cdot \frac{\psi}{\Omega} \quad (\text{II-33})$$

Here σ_{12} is the shear stress, R the cone radius, Ω the angular velocity and ψ the angle between the cone and the plate.

The second normal stress difference can be measured by combining experiments of the cone and plate and the parallel plate viscometers; but this will not be discussed here as it was not pursued in the present work. For experimental studies of this type we cite the studies of Ginn and Metzner (61, 62) on polymer solutions and Lee and White (97) on melts.

Above certain critical shear rate, the polymer melt starts to flow out of the gap between the cone and the plate. This phenomena has been observed by several research groups (76, 90, 12, 36).

Capillary Viscometer. The use of cone-and-plate viscometer is limited to low shear rate, below about 10 sec^{-1} , due to the flow instability mentioned above. At high shear rates, a capillary type of viscometer can be used. It consists of a long capillary tube through which a fluid is passed under a measured pressure drop. Several commercial machines of this type are available.

The shear rate in the capillary rheometer is determined from Weissenberg equation (45, 110).

$$\dot{\gamma}_w = \frac{3n' + 1}{4n'} \cdot \frac{32Q}{\pi D^3} \quad (\text{II-34})$$

$$n' = \frac{d \log(\sigma_{12})_w}{d \log\left(\frac{32Q}{\pi D^3}\right)} \quad (\text{II-35})$$

Here Q is the volumetric flow rate, D is the capillary diameter and $(\sigma_{12})_w$ is the shear stress at the wall, which is determined from the plot of total pressure drop across the capillary die versus L/D ratio for a series of dies at the same shear rate (8, 12).

$$\Delta P_T = \Delta P_E + 4(\sigma_{12})_w \frac{L}{D} \quad (\text{II-36})$$

Here L is the length of the capillary die and ΔP_E is the entrance pressure drop. Very large pressure drops have been observed in polymer melts and solutions (12).

Nylon-6

Nylons are condensation polymers and their molecular weights are much smaller (usually in the range of 15,000 to 30,000) compared to polyolefins (molecular weight 50,000 to 500,000). Not unexpectedly, nylon melts exhibit flow behavior more similar to Newtonian liquids. Pezzin and Gechele (128) showed that the viscosity of nylon-6 melts changes only slightly with shear rate. They published experimental results on the rheological properties of nylon-6 melts of different molecular weights at various temperatures and levels of moisture content. The activation energy of viscous flow was found to be 9 to 13 K cal/mol and to be independent of molecular weight. Westover (171) has published shear stress-shear rate and viscosity shear rate data on nylon-6 melts. An

activation energy of 11 K cal/mol can be calculated from this data.

Pezzin and Gechele (128) also established the validity of 3.4 power law in the viscosity molecular weight relationship of nylon-6 melt beyond certain critical molecular weight.

This critical molecular weight has been reported by Fox and Loshaek (55) and Fox, Gratch and Loshaek (54) to be 5,230 for nylon-6.

Schaeffgen and Flory (140) obtained viscosity molecular weight relationships for specially prepared mono, di, tetra and octa chain poly (ϵ -caprolactam) samples. They obtained linear relationships when log of melt viscosity was plotted against the square root of molecular weight. The same data, when replotted as log (viscosity) versus log (M_w), gave lines of 3.5 slope (94). The critical molecular weight was higher for octa chain polymers than any other polymers studied.

Kotliar (95) has collected data on melt viscosity of nylon-6 at 250°C and various shear rates in the Instron rheometer and plotted as a function of intrinsic viscosity of extruded polymer. He found a relationship of the form

$$\eta_{\text{Melt}} = A[\eta]^B \quad (\text{II-37})$$

where A and B are constants which depend on the shear rate but lie in the range of 6000-1000 and two to six respectively.

Little is known of melt elasticity of nylon-6. However, this may be small because of its low molecular weight. In private communications from J. H. Southern (145) the ratio of first normal stress difference to shear stress at shear rate of 10 sec^{-1} and temperature of

230°C has been reported to be 0.016 for nylon-6. This is much less than that for polyolefins.

C. CRYSTALLINE ORIENTATION

General

The crystalline orientation is an important aspect of many polymer processes. The degree of orientation of crystals relative to the machine direction affects the mechanical and the optical properties of the processed polymer. For example, the tensile strength of fibers increases tremendously after orienting the polymer molecules along the fiber axis by the process of drawing. Quantitative evaluation of orientation is, therefore, important. Hermans (69) has defined a coefficient of axial orientation. This was later modified by Ziabicki (186). He defines it as "a ratio of the resultant polarization anisotropy of a given fibrous system to the theoretical polarization anisotropy of the system consisting of ideally extended and axially parallel macro molecules where the adding up of constituent polarization anisotropies of the individual structural elements is carried out geometrically, exclusively, neglecting the possible changes of internal field."

In mathematical form,

$$f = \frac{(\alpha_{11} - \alpha_1)}{\alpha_1 - \alpha_2} \quad (II-38)$$

For rigid crystallites, Hermans has shown, using "Polany's Sphere" construction that (69)

$$f = 1 - \frac{3}{2} \overline{\sin^2 \phi} = \frac{3 \overline{\cos^2 \phi} - 1}{2} \quad (\text{II-39})$$

where $\overline{\sin^2 \phi}$ and $\overline{\cos^2 \phi}$ are the average sine squared and cosine squared values of the angle ϕ between the reference direction and the chain direction. The value of f is 0, 1 or $-1/2$ for random orientation, orientation parallel to the reference direction, or orientation perpendicular to the reference direction, respectively.

Stein and Norris (153) and Stein (154) have discussed the application of Equation II-39 explicitly to polyethylene crystals. They have used Equation II-39 to define orientation factors for the a- and b-axes as well as the c-axis (chain direction). It is useful to determine orientation functions for all three crystallographic axes, since this provides much more information about the detailed orientation and morphology of the crystals in the sample than knowing the chain axis orientation factor alone.

For cubic, tetragonal or orthombic crystal systems, all the three crystallographic axes are mutually perpendicular and the orthogonality relationship exists.

$$\overline{\cos^2 \phi_a} + \overline{\cos^2 \phi_b} + \overline{\cos^2 \phi_c} = 1 \quad (\text{II-40})$$

where ϕ_a , ϕ_b and ϕ_c are the angles the three axes make with the reference direction. Hence,

$$f_a + f_b + f_c = 0 \quad (\text{II-41})$$

Thus, in systems which have orthogonal crystal axes, the three orientation functions are not independent, and only two of them are required to characterize the orientation.

The values of $\overline{\cos^2 \phi}$ required for the determination of two of the three orientation functions can be obtained from the intensities of x-ray diffraction patterns. For example, to determine $\overline{\cos^2 \phi_a}$, one needs to have the azimuthal distribution of intensity of x-rays diffracted from the set of planes which are perpendicular to the a-axis, viz(hoo) planes.

$$\overline{\cos^2 \phi_a} = \frac{\int_0^{\pi/2} I_{hoo} \cos^2 \phi_a \sin \phi_a d\phi_a}{\int_0^{\pi/2} I_{hoo} \sin \phi_a d\phi_a} \quad (II-42)$$

Wilchinsky (176) has generalized the analysis of orientation functions to non-orthogonal unit cells. This analysis could be used to determine the orientation function of a certain crystallographic axis even when reflections from the set of planes which are perpendicular to this axis are not available. This analysis has been used by Wilchinsky (177) and Hoshino, et al. (96) and Samuels (136) to obtain the orientation functions of polypropylene films. The application of Wilchinsky's analysis to various melt-spun fibers is discussed in a future section.

Nylon-6

There have been very few papers in the open literature on quantitative determination of crystalline orientation functions of

nylon-6. Sakaoku, Marosoff and Peterlin (134) reported measurements of chain axis orientation of drawn nylon-6 bristles. Wilchinsky's analysis was applied. They used (200) and combined (002), (202) reflections of monoclinic nylon-6 crystals for this purpose. The chain axis orientation factor increased from 0.83 to 0.97 when the draw ratio of nylon fibers increased from 2 to 4.95.

D. MELT SPINNING

Initial Conditions--Die-Swell and Melt Fracture

Two important phenomena are observed when a polymer melt flows through a capillary: the die-swell and the melt fracture. When a polymer melt emerges out of a die, it swells. The extent of swelling of a viscoelastic fluid depends on shear rate, L/D ratio and the viscoelastic nature of the material (11, 117). Several theories have been proposed to explain the die-swell effect (129, 191, 107, 6, 11, 148). The die-swell is also suggested to be due to the unconstrained elastic recovery (51, 146, 117). However, in melt spinning process, the elastic recovery is not unconstrained. The melt recovers from Poiseuille shearing flow to a state of uniaxial stress. This view has been taken by White and Roman (173) who developed an equation for the die-swell ratio for an extrudate under the influence of tensile force.

When a polymer melt is extruded at high shear stress, the extrudate becomes distorted either in the form of uneven swell of varying period or of a screw thread. This phenomena, called melt fracture has been studied by several authors (147, 161, 162, 17). The origin of instability is found in some cases to be at the entrance of

the die. Melt fracture occurs at a critical value of shear stress, of the order of 10^6 dynes/cm² (147, 161, 17). This critical value varies inversely with weight average molecular weight (147, 9, 10). Generally one operates at extension rates below the extrudate distortion conditions.

Dynamics

Although the studies of melt spun fibers began in 1932 with the efforts of Carothers and Hill (30), a serious study of both theoretical and experimental aspects of melt spinning process was started by Ziabicki and Kedzierska (188, 189, 190, 191, 192, 193) in 1959-60. They used the framework of continuum mechanics to formulate the governing equations of mass, momentum and energy balance in the spinline. The continuity equation was expressed as (190)

$$A \cdot v \cdot \rho = W = \text{constant} \quad (\text{II-43})$$

where A is the fiber cross sectional area, v the fiber velocity, ρ the fiber density, and W the mass flow rate.

The force balance on the spinline between any position X and the position L (at the take-up device) was expressed as (188)

$$F_{\text{ext}}(L) = F_{\text{rheo}}(x) + F_{\text{drag}}(x) - F_{\text{gravity}}(x) + F_{\text{inertia}}(x) \quad (\text{II-44})$$

where

F_{ext} = external force applied at the take-up device.

F_{rheo} = rheological force.

F_{drag} = aerodynamic drag on the filament.

F_{inertia} = inertial force.

F_{gravity} = gravity force

The surface tension force was found to be negligibly small. For a given mass flow rate, the gravity force is significant at low take-up speed whereas the drag and the inertia forces become important at high take-up speeds.

Several papers have been published on the assessment of aerodynamic drag on a running filament. Sakiadis (135) used laminar and turbulent boundary layer analysis to calculate the drag on a cylinder of a constant diameter running through a stationary medium at a constant velocity. The drag force was expressed in terms of a so-called momentum area as a function of a parameter ξ

$$F_{\text{drag}} = \rho v^2 \theta, \quad \theta = f(\xi) \quad (\text{II-45a})$$

where

$$\xi = 8(\text{Re}_x)^{1/2}/\text{Re}_d = 8\left(\frac{vx}{vd^2}\right)^{1/2} \quad (\text{II-45b})$$

Re_x and Re_d are the Reynold's numbers based on the length and the diameter of the cylinder.

Andrews (4) studied experimentally the air-drag on a stationary

filament in a wind tunnel. His results in terms of friction factor and the Reynold's number Re can be expressed as

$$C_f = 1.30(Re_d)^{-0.61} \quad (II-46)$$

However, it is doubtful if the wind-tunnel experiments of Andrews are really equivalent to the running spinline.

Sano and Orii (138) and Hamana, Matsui, Kato (64) measured tension at various points of a solidified running filament and obtained C_f - Re relationship as

$$C_f = 0.68 Re_d^{-0.8} \quad \text{Sano and Orii} \quad (II-47)$$

$$C_f = 0.37 Re_d^{-0.61} \quad \text{Hamana, et al.} \quad (II-48)$$

These results give almost the same values of C_f in the range of Re_d of ten to fifty.

Aoki, Suzuki and Ishimoto (5) did experiments apparently similar to those of Andrews and obtained

$$C_f = 0.18 Re_d^{-0.44} \quad (II-49)$$

This gives friction factors approximately equal to those of Hamana, et al.

It may be noted that the frictional drag predicted by Andrews' experiments is quite high compared to the predictions of other workers.

Rheological Aspects of Isothermal Spinning

Going back to the force balance Equation II-44, the rheological force is constant when the combined drag and inertia forces are equal to the gravity force. For such a case, the equation of force balance and continuity could be combined with a suitable rheological equation to obtain the diameter and the velocity profile along the spinline. For a Newtonian fluid, under isothermal conditions, Ziabicki has obtained these profiles as (190)

$$v(x) = v_0 \exp[F_{\text{rheo}} \cdot x/\chi Q] \quad (\text{II-50})$$

$$d(x) = d_0 \exp[-F_{\text{rheo}} \cdot x/2\chi Q] \quad (\text{II-51})$$

where χ is the elongational viscosity defined by

$$\chi = \frac{F_{\text{rheo}}/A}{dv(x)/dx} \quad (\text{II-52})$$

Experimental studies of melt spinning of Newtonian fluids have been carried out by some investigators (188, 87, 108). $\chi = 3\eta$ relationship has been obtained in these experiments.

Acierno, et al (2), Chen, et al. (39) and Han and Lamonte (66) have experimentally obtained $\chi - \dot{E}$ relationships in isothermal melt spinning of viscoelastic fluids. For LDPE, χ increases with $\dot{E}$ but for HDPE and polypropylene, χ either decreases or remains constant.

Most of the synthetic fibers are made from viscoelastic polymers and as such an appropriate constitutive equation must be used in the

study of rheological aspects of spinning. The first attempts to apply the concepts of viscoelastic fluid theory to fiber spinning was made by White (172) and by Matovich and Pearson (103). Recently, more rigorous formulations (such as Equation II-18 with $m_2 = 0$) have been applied with partial success to the melt spinning process under isothermal conditions by Acierno, et al. (2), and later by Chen, et al. (38). In their analysis the basic idea of elongational viscosity χ (Equation II-52) was retained. This equation is strictly true for the steady elongation with constant elongation rate. In isothermal melt spinning, the elongation rate varies significantly along the spinline.

More recently, Denn, Petrie and Avenas (49) used a generalized Maxwell model and combined it with equations of continuity and momentum to obtain a single differential equation for $v(x)/v(0)$ which they denote $u(\xi)$. This is

$$\frac{u}{du/d\xi} - 3\epsilon + \alpha u - \alpha \frac{u^2 d^2 u/d\xi^2}{(du/d\xi)^2} - 2\alpha^2 u \, du/d\xi = 0 \quad (\text{II-53})$$

where $\xi = x/L$, $\alpha = \tau v_0 / L$, the Weissenberg number, and $\epsilon = \eta Q / FL$.

They obtained both asymptotic solutions and a general numerical solution of Equation II-53. They used this equation to predict the polymer relaxation time from the spinning data. The predicted relaxation times were 20 to 80 percent larger than those obtained with a Weissenberg rheogoniometer.

Non-Isothermal Spinning

Although the isothermal melt spinning is better for studying the

influence of rheological properties in melt spinning, the industrial melt spinning process takes place under non-isothermal conditions. Here the effects of temperature variation in the spinline become more important, and the heat balance equation must be simultaneously solved with the force balance equation. Kase and Matsuo (84, 85) made a simple one dimensional heat balance on a differential element of the spinline, neglecting radiation and heat of crystallization. Their steady state heat balance equation is

$$dT/dx = - \frac{2\sqrt{\pi A}}{GC_p} h(T - T_a) \quad (\text{II-54})$$

where

dT/dx = the temperature gradient.

A = the area of cross-section.

G = the mass flow rate.

h = the heat transfer coefficient.

T_a = the ambient temperature.

C_p = the heat capacity.

The relationship between the Nusselt number hd/k and the Reynolds' number $\frac{dv\rho_a}{\mu_a}$ was obtained experimentally by Kase and Matsuo (84) by blowing air over a hot wire. They found:

$$\frac{hd}{k} = 0.42 \left(\frac{dv\rho_a}{\mu_a} \right)^{1/3} (1 + K) \quad (\text{II-55})$$

where K is a function of the ratio of velocity of air flow in the transverse direction to the filament velocity. The force balance equation used by Kase and Matsuo is the same as the equation of Ziabicki discussed earlier for a constant rheological force. This is expressed as

$$\frac{dA}{dx} = -\frac{F \cdot \rho}{G_x} A \quad (\text{II-56})$$

Kase and Matsuo combined Equations II-54 through II-56 and solved numerically using experimental data for C_p , ρ and χ . The solution was used to study the effect of various spinning variables on the profiles of temperature and area of cross-section of the filament. They obtained good agreement with the experimental profiles. Lamonte and Han (96) have also studied the theoretical and experimental aspects of rheology and heat transfer. Empirical equations were used to consider dependence of χ on temperature and elongation rate.

Acierno, et al (2) have computed heat transfer coefficient of a descending fiber, using dimensional analysis and an integral boundary layer analysis of forced convection from the fiber. They obtained a correlation between the local Nusselt number and Reynold's number.

None of the above authors has taken phase transformation into consideration. Nakamura and co-workers (118) included heat of crystallization in the energy balance equation and obtained an expression relating crystallinity to temperature. Morrison (115) simultaneously solved heat transfer and phase transformation equations with the help of numerical techniques to obtain temperature profiles as a function of

fiber radius and axial distance, but he neglected crystallization kinetics.

In experimental studies of non-isothermal melt spinning, $\chi(T)$ function was obtained by Kase and Matsuo for PET (84) and polypropylene (85) and by Hamana, Matsui and Kato (64) and Hill and Cucalo (72) for PET.

Structure Development

As pointed out in Section C, the formation of structure, i.e., crystallinity, orientation and morphology during melt spinning is important in determining mechanical and optical properties of fibers.

As early as 1932, Carothers and Hill (30) noted the effects of spinning variables like fiber tension on the x-ray diffraction patterns of polyamides and polyesters. They correctly attributed these to the molecular orientation. Keller (88) in 1956 discussed qualitatively the orientation and crystallinity in melt spun fibers and gave supporting x-ray data from nylons, polyethylene and polyethylene terephthalate. Hearle (67) investigated crystalline structure of fibers, but he did not deal with the spinning process as such. Ziabicki (189, 192, 193) used the techniques of birefringence and x-ray diffraction to study the effects of spinning parameters on the molecular orientation of nylon fibers. He found that the orientation of molecules increased with increase in take-up stress, parallel velocity gradient and inverse of fiber diameter (measure of cooling rate). Abbott and White (1) studied melt spinning of low and high density polyethylene and examined variation of orientation and crystallinity in the spun fibers with spinning speed, melt flow rate and melt temperature. The modulus and tensile

strength of the final fibers were found to increase with increasing crystalline orientation.

Crystallization process in the melt spinning of nylon 66 fiber was studied by Chappel and co-workers (35) using direct x-ray diffraction analysis of spinline and also by techniques of depolarization of light and microscopy. The effect of moisture on crystalline character was observed. Katayama, Amano and Nakamura (86) used similar techniques along with fiber surface temperature and diameter measurements to study structure development during melt spinning of polyolefin fibers. They observed an increase in crystallization rate due to molecular orientation and also found a morphology consisting of lamellar and interlamellar regions stacked normal to the fiber axis.

Ishikawa (83) studied the morphology of polyethylene fibers using special compression and stretching techniques combined with x-ray diffraction methods. He observed differences in morphology in fibers spun under different spinning conditions. From the electron micrographs of polyethylene fiber surface, Fung and Carr (57) concluded the presence of row nucleated structure caused by orientation of melt during draw-down. They concluded that a stress induced morphology was produced by a skin-core effect in the solidifying fiber. Birefringence measurement made across the diameter of the fiber showed higher orientation at the fiber surface than at the center.

More recently Dees and Spruiell (48) and Henson (68) made an online x-ray diffraction study of polyethylene and polypropylene spinline at different take-up velocities. The x-ray patterns were used to study the development of crystallinity along the spinline.

Hermans-Stein orientation functions were obtained for all the three crystallographic axes of polyethylene (48). Wilchinsky's analysis was used in the case of polypropylene (68).

When plotted as a function of take-up velocity, the b-axis orientation function f_b quickly dropped to about -0.4 and remained at this level. The f_c function slowly increased from 0 and approached values of about 0.6 at the highest take-up velocities investigated. For polyethylene, f_a first increased to about + 0.25 and then decreased and approached - 0.5 as the take-up velocity was increased. This indicated that the b-axis was perpendicular to the fiber axis and the c-axis slowly became more parallel to the fiber axis as the take-up velocity was increased. Based on these studies, it was concluded that the morphology in the spinline changed from spherulitic at low take-up velocity to a row nucleated twisted lamellae structure at intermediate velocities and finally to row nucleated structure with less twisted lamellae at high take-up velocities.

For different extrusion temperatures, the plots of f versus take-up velocity were separated from each other. When these factors were plotted as a function of spinline stress for polypropylene (68), it was found that fibers spun under different spinning conditions lay on the same curves. The orientation function-spinline stress plots obtained by Khokhani (89) for polyoxymethylene fibers spun at different extrusion rate also lay on the same curves.

Nadella (116) obtained similar results when he plotted orientation factors for polypropylene of different molecular weights as a function of spinline stress. This was clear evidence that the

morphology developed during melt spinning is determined primarily by the spinline stress.

Nylon-6

Melt spinning studies of nylon-6 have been reported by several investigators. Hamana, Matsui and Kato (64, 65) obtained diameter, temperature and birefringence profiles in the spinline of nylon-6 as well as polyethylene terephthalate. Effects of changing mass flow rate and take-up velocity were observed. At high take-up velocity, birefringence in the spinline was found to increase even though the fiber diameter remained constant after solidification. Birefringence was found to increase when the dry, spun fibers were conditioned at 65 percent R. H. X-ray diffraction patterns of the dry, spun fibers showed amorphous halo; which changed to partially crystalline after conditioning.

Profiles of diameter and temperature were compared with theoretical profiles obtained by numerically solving the mass momentum and energy balance equations. Fairly good agreement was obtained. They also obtained elongational viscosity as a function of temperature.

Similar studies were carried out by Ishibashi, Aoki and Ishii (81) on nylon-6. Effects of melt temperature, polymer molecular weight, extrusion rate and take-up velocity were studied on the profiles of diameter and temperature. The relationship between the elongational viscosity and fiber surface temperature was experimentally obtained.

No attempt has been made by above authors to take the visco-elastic nature of the polymer into account. Also no studies have been

reported on detailed rheology of isothermal spinning of nylon-6 as well as on the structure development during melt spinning of nylon-6.

Very few papers have appeared in the open literature on the studies of die-swell behavior and melt fracture of nylon-6. Ziabicki (191) studied effects of various parameters on die-swell of nylon-6. Increase of spinneret diameter, mass flow rate or decrease of spinneret length (all of this is equivalent to reducing the residence time for flow in the spinneret) resulted in increased die-swell. The die-swell also increased when the extrusion temperature was reduced below 255°C. The take-up velocity was found to have negligible effect on the die-swell.

Ishibashi (82) has carried out experimental work on the die-swell behavior of nylon-6 melts. His data correlate well with an equation

$$\frac{\tau_s}{T} = 4.4[(d/d_0)^4 - (d_0/d)^2] \quad (\text{II-57})$$

where τ_s is the shear stress, T is the absolute temperature and d/d_0 is the die-swell ratio. This equation was obtained from the theory of rubber elasticity.

The irregularity of extrudate surface of nylon-6 was also studied by Ziabicki (191). For a shear rate of 550 sec^{-1} , the irregularity appeared when the extrusion temperature was as low as 220°C and it disappeared when either the extrusion temperature was increased or the shear rate was decreased.

E. POST TREATMENT AND MECHANICAL TESTING OF SPUN FIBERS

General

Post treatment of spun fibers includes several processes such as drawing, twisting, annealing, etc. The processes of drawing and twisting are beyond the scope of this dissertation. However, drawing as it occurs during mechanical testing of spun fibers as well as annealing of spun fibers will be discussed in this section.

Annealing. Annealing of fibers causes several changes in their structural characteristics and properties. Studies of annealing of as-spun fibers are rare, although a few papers have been published on the effects of annealing on various drawn fibers such as polyamides (70, 71, 15), polyesters (70, 152, 52) and polyurethane fibers (183). The most pronounced effects are on the SAXS. The long period of the crystallites as well as the intensity of the SAXS is increased by annealing. The WAXS showed little change in the crystalline orientation, but the crystalline order increased (15, 52). According to Clark (39) and Sprague (149), the annealing treatment perfects the row structure developed during spinning.

Annealing also causes changes in the crystalline forms of polymorphous materials. Again, no studies on spun fibers are reported, but changes in drawn polypropylene films from paracrystalline to crystalline forms have been studied by Wyckoff (179).

Mechanical Testing. During mechanical testing, a fiber sample is held between two jaws, one of which moves at a constant speed. A

typical load-elongation response of spun fibers consists of initial stress build up region where Hooke's law applies, followed by a yield point where fiber usually necks down. Here a considerable fiber deformation occurs for a relatively small increase in stress. A further increase in strain accompanies a continuous increase in stress until the sample ruptures.

Mechanical properties of as-spun polyethylene fibers have been studied by Abbott and White (1), Dees and Spruiell (48), White, Dharod and Clark (175) and Sze, Spruiell and White (157). Similar studies for polypropylene fibers have been made by Henson (68) and Nadella (116); and for polyoxymethylene fibers by Khokhani (89). The filaments spun at low take-up velocity showed a yield point and necking. The natural draw ratio decreased with increase in take-up velocity, and at the highest take-up velocities studied, the fiber exhibited neither yield point nor necking. The crystalline orientation of the material in the necked region was considerably greater than that in the remainder of the fiber (175). The modulus and the tensile strength increased with take-up velocity, but elongation to break decreased. A strong correlation was observed between these properties and the initial c-axis orientation factor in the spun fibers (as well as the spinline stress) (1, 48, 68, 89, 116).

It may be pointed out at this stage that the response of fibers to mechanical testing depends on the strain rate. Butterworth and Abbott (28) have shown that nylon 66 yarn showed higher modulus and lower elongation to break when tested at higher strain rate.

Physical properties of fibers are affected by annealing treatment

spacing of the fibers were determined from WAXS and SAXS. Mechanical properties were obtained for samples exposed to 65 percent relative humidity for 24 hours.

Small Angle X-Ray Scattering

SAXS patterns were obtained using a Kiessig camera with pin-hole collimation. The camera was mounted on the Rigaku rotating anode x-ray generator. The camera was evacuated by a mechanical vacuum pump to reduce air scattering. Film to sample distance of 400 mm was used. Exposure time of ten hours was used.

Wide Angle X-Ray Scattering

To obtain WAXS patterns on a spun filament, the same Kiessig camera was used, but this time the sample to film distance was reduced to 98 mm by eliminating the extension tube used in SAXS studies.

X-Ray Diffractometers

An XRD-5 General Electric X-Ray Diffractometer was used to get 2θ scan of the as-spun filaments and also treated fibers. Fibers were wound on an H-frame in a parallel arrangement. A slit collimation was used to collimate the x-rays. This instrument was also used for quantitative evaluation of orientation factors. Orientation factors for different hkl planes could be obtained. For this purpose the 2θ value for an hkl plane was experimentally determined and the diffractometer was set at this 2θ value. The sample was then rotated through the angle from equator to meridian in steps of 2.5 degrees and intensity of the diffracted beam at each angle was measured in counts using a

$$f_c = -2f_a$$

(III-13)

These orientation factors were obtained for fibers spun at different take-up velocities.

Mechanical Properties

A table model Instron Tensile Testor maintained by the U. S. Department of Agriculture was used to obtain the force-elongation data for fibers spun at different take-up velocities. All tests were made after conditioning the samples at 65 percent relative humidity and 20°C for 24 hours. The tests were also made at the same conditions. The conditioning room was also maintained by the U.S.D.A.

Tensile strength, elongation at break and initial modulus were obtained from the force-elongation data. A gauge length of one inch and the crosshead speed of one inch/minute were used.

CHAPTER IV

RHEOLOGICAL CHARACTERIZATION

A. MELT VISCOSITY

Results

The melt viscosity of dry nylon-6 samples was determined at three different temperatures, 230°C, 250°C, and 270°C. The Weissenberg rheogoniometer was used for viscosity measurements in the shear rate range of 0.1 to 20 sec^{-1} , and the Instron capillary rheometer was used in the shear rate range of 50 sec^{-1} to 1000 sec^{-1} . Although a "dry" nitrogen atmosphere was maintained in the rheogoniometer, it was observed at the end of the experiments that the polymer had changed its appearance from white to dark brown or black. This was observed mainly at the outer edge of the polymer sample. The polymer within the gap remained almost the same in appearance as the original sample. It was thus evident that some of the polymer degraded during the experiment.

The viscosity results for the nylon-6 are shown in Figure IV-1. The viscosity was constant at low shear rates. Zero shear viscosity was of order 10,000 poise at 230°C, 5000 poise at 250°C and 3300 poise at 270°C.

Discussion

The rheogoniometer data show that the viscosity of nylon-6 is constant up to a shear rate of about 5 sec^{-1} . The results from the

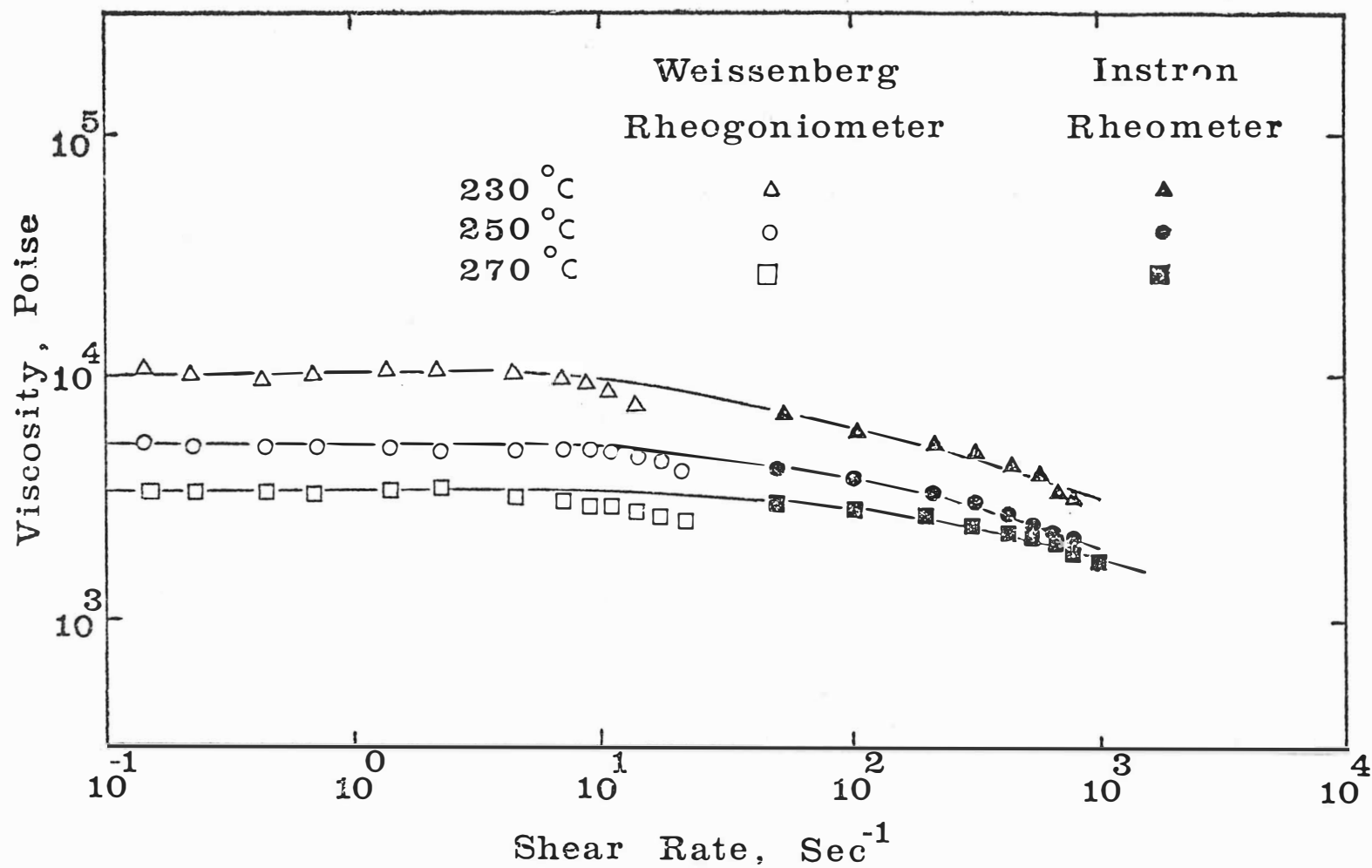


Figure IV-1. Shear viscosity of nylon-6 melts as a function of shear rate.

rheogoniometer and the rheometer seem to match very close with each other (Figure IV-1). A continuous curve could be drawn through all the points except a few lying in the shear rate range of 5 sec^{-1} to 20 sec^{-1} . The viscosity in this range of shear rates lies under the respective curves. In this range of shear rate a flow instability was observed in the Weissenberg rheogoniometer. The melt at these shear rates flowed out of the gap between the cone and the plate and consequently lower viscosity.

It is also possible that the reduction in viscosity in the shear rate range of 5 sec^{-1} to 20 sec^{-1} is due to the chemical degradation of the sample. In order to check this, the viscosity was measured on the same sample first at increasing shear rate and then at decreasing shear rate. If degradation occurs, the viscosity should be lower in the latter case. No detectable change was observed when measurements were made at 230°C and 250°C . A slight decrease of viscosity was observed at 270°C . Thus it can be argued that the reduction in viscosity at $5\text{-}20 \text{ sec}^{-1}$ was due to combined effect of flow instability and chemical degradation at 270°C but only due to flow instability at 230°C and 250°C .

In Figure IV-2, the viscosity behavior of nylon-6 samples used in this work is compared with the results obtained by Pezzin and Gechele (128) and Kotliar (95) on their nylon-6 samples. Both the investigators reported viscosity results on nylon-6 samples of various molecular weights or intrinsic viscosities. Only those samples are selected here for comparison purpose which have characteristics similar to the nylon-6 used in the present studies. These characteristics

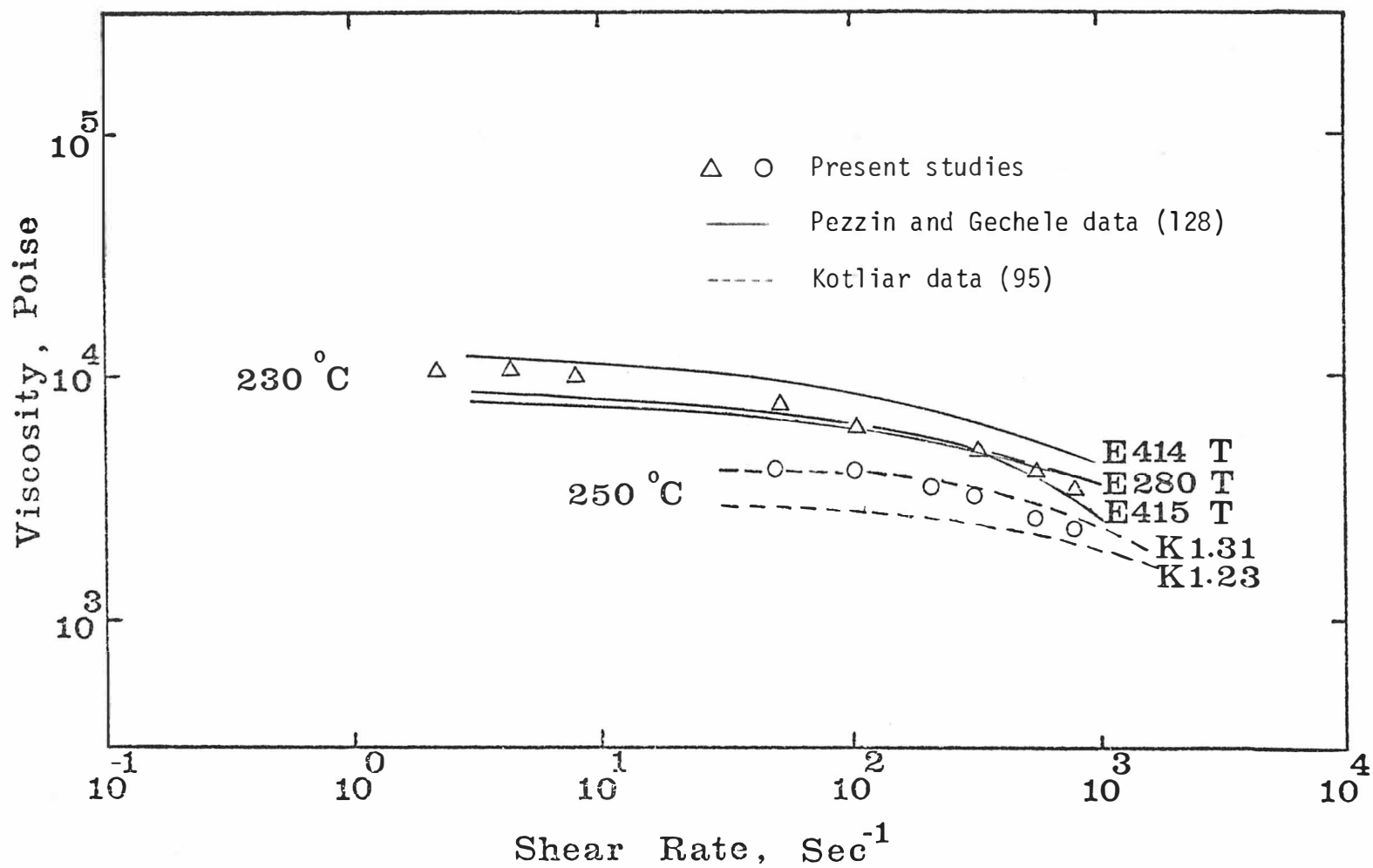


Figure IV-2. Comparison of shear viscosity-shear rate relationships of different nylon-6 melts.

are shown in Table 4.

The moisture content of the samples is an important factor in the measurement of viscosity. The moisture content of the samples selected from the work of Pezzin and Gechele is less than 0.15 percent. Kotliar did not report the moisture content. Nevertheless, the viscosity-shear rate relationships of all nylon-6 samples are similar quantitatively and qualitatively. In Figure IV-3 we have compared the viscosity of nylon-6 at 230°C with that of LDPE at 180°C obtained by Chen and Bogue (37) and Ballenger, et al. (12). A marked difference is observed. The viscosity of LDPE drops sharply from its initial value of more than 10^5 poise, as the shear rate is increased. It crosses over the viscosity of nylon-6 beyond a shear rate of about 200 sec^{-1} . The viscosity of nylon-6 is quite low initially and it remains constant up to a shear rate of about 10 sec^{-1} and then drops comparatively slowly. The difference in the viscosity behavior of polyamides and polyolefins is thus obvious.

B. PRINCIPAL NORMAL STRESS DIFFERENCE

Results

The principal normal stress difference N_1 was also measured in the shear rate range of 0.1 sec^{-1} to 20 sec^{-1} , using the Weissenberg rheogoniometer. However, in the low shear rate region (0.1 sec^{-1} to 4 sec^{-1}) N_1 was found too small to be measured accurately. Hence these results are reported only in the shear rate range of 4 to 20 sec^{-1} . From these results the first normal stress difference coefficient ($\psi_1 = N_1/\dot{\gamma}^2$) was calculated. The relaxation time ($\tau = \frac{N_1}{2\sigma_{12}\dot{\gamma}}$) was calculated using the viscosity and the normal stress results. These are

TABLE 4
CHARACTERISTICS OF NYLON-6 SAMPLES USED BY DIFFERENT INVESTIGATORS

Investigator	Sample Designation	$\bar{M}_n$	$[\eta]$ dl/g	Moisture Content	Temperaure of Measurements °C
Bankar	Δ	23,000	≈ 1.24 at 20°C	0.03%	230
	$\square$				250
Pezzin and Gechele	E 280 T	20,000	1.27 at 25°C	< 0.15%	230
	E 414 T	22,300	Not reported		
	E 415 T	22,900	Not reported		
Kotliar	K 1.23	Not reported	1.23	Not reported	250
	K 1.31		1.31		

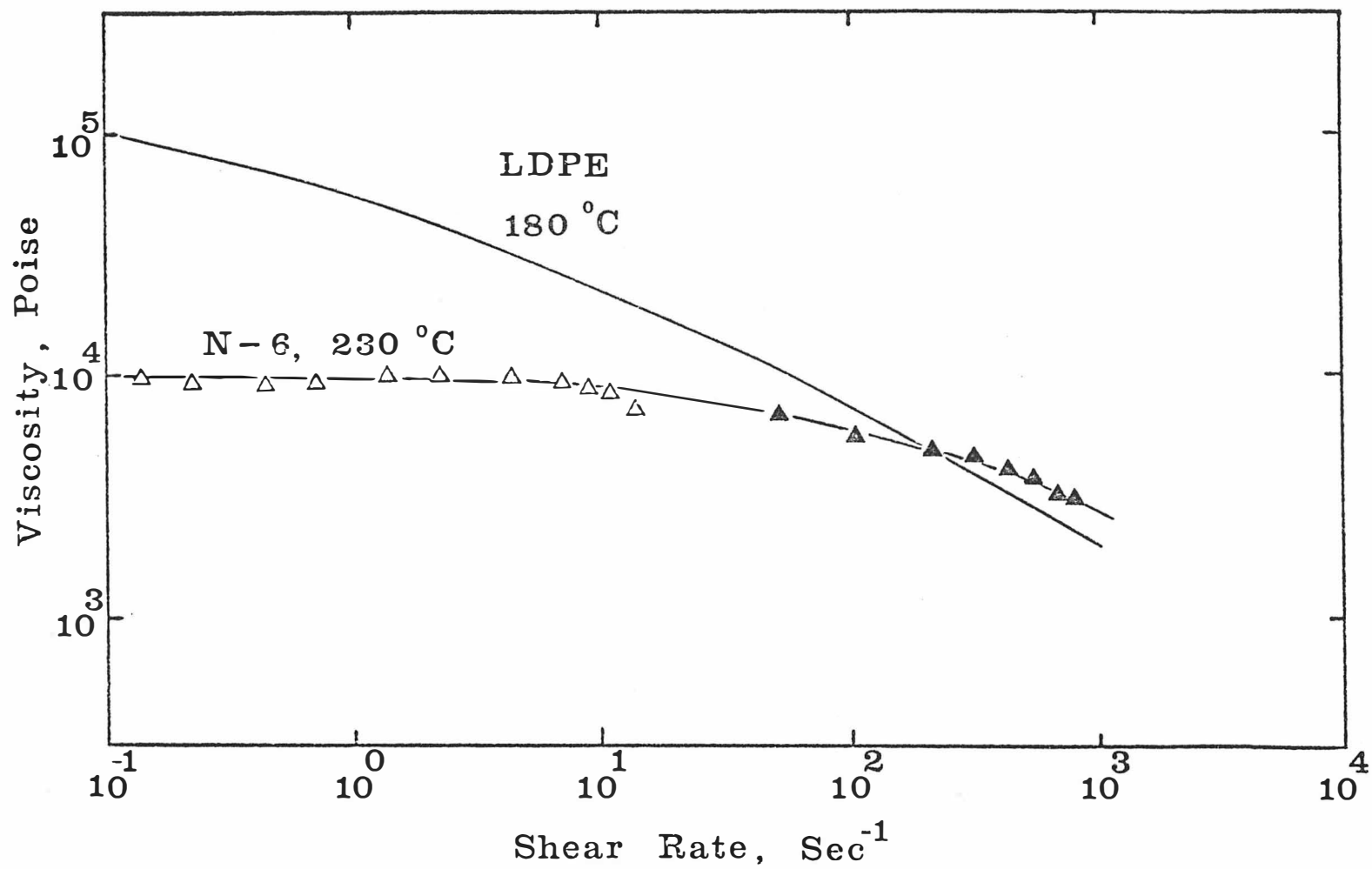


Figure IV-3. Shear viscosity-shear rate relationships of nylon-6 and low density polyethylene melts.

plotted in Figures IV-4 and IV-5 as a function of shear rate and are shown by unfilled points. The average values of τ are about 0.034 seconds at 230°C, 0.014 seconds at 250°C and 0.009 seconds at 270°C.

Discussion

ψ_1 and τ are reported in the shear rate range of 4-20 sec^{-1} where flow instability was observed. Hence these are only the "apparent" values of the first normal stress difference coefficient and the relaxation time. "True" values of these parameters can be calculated using Figure IV-1. In Figure IV-1, the continuous curves were assumed to show true value of viscosity. The experimental points in the shear rate range of 4-20 sec^{-1} do not lie on the curves and are therefore only apparent values of viscosity. Thus we can write Equations II-30 and II-31 as

$$\sigma_{12_T} = \eta_T \dot{\gamma} = \frac{3T}{2\pi R^3} \quad (\text{IV-1a})$$

$$\sigma_{12_{\text{App}}} = \eta_{\text{App}} \dot{\gamma} = \frac{3T}{2\pi (R-\Delta)^3} \quad (\text{II-1b})$$

$$N_{1_T} = \psi_{1_T} \dot{\gamma}^2 = \frac{2F}{\pi R^2} \quad (\text{IV-2a})$$

$$N_{1_{\text{App}}} = \psi_{1_{\text{App}}} \dot{\gamma}^2 = \frac{2F}{\pi (R-\Delta)^2} \quad (\text{IV-2b})$$

The subscripts "T" and "App" indicate true and apparent values of the parameters respectively. $(R-\Delta)$ is the effective radius up to which

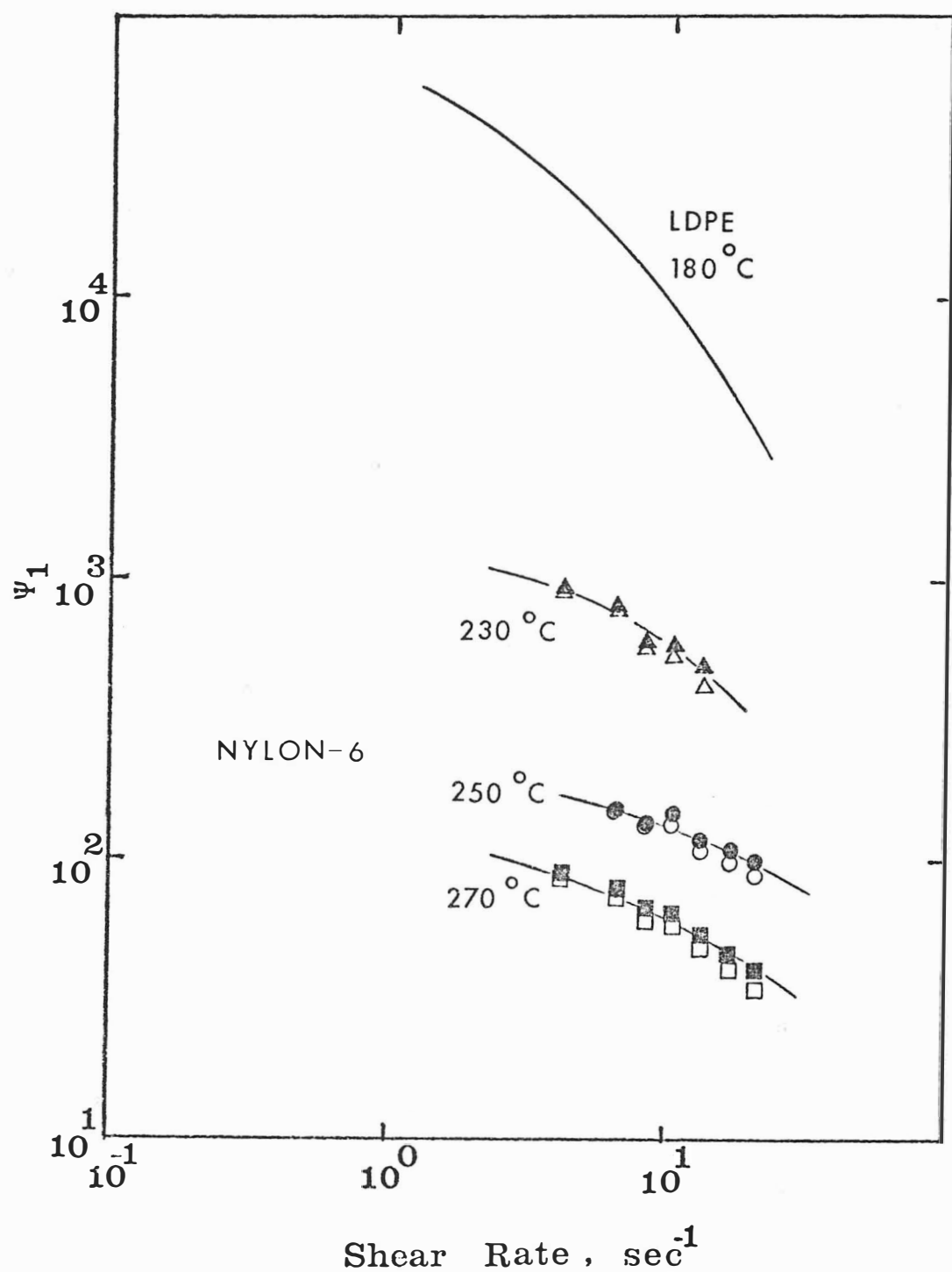


Figure IV-4. First normal stress difference coefficient of nylon-6 and low density polyethylene melts as a function of shear rate.

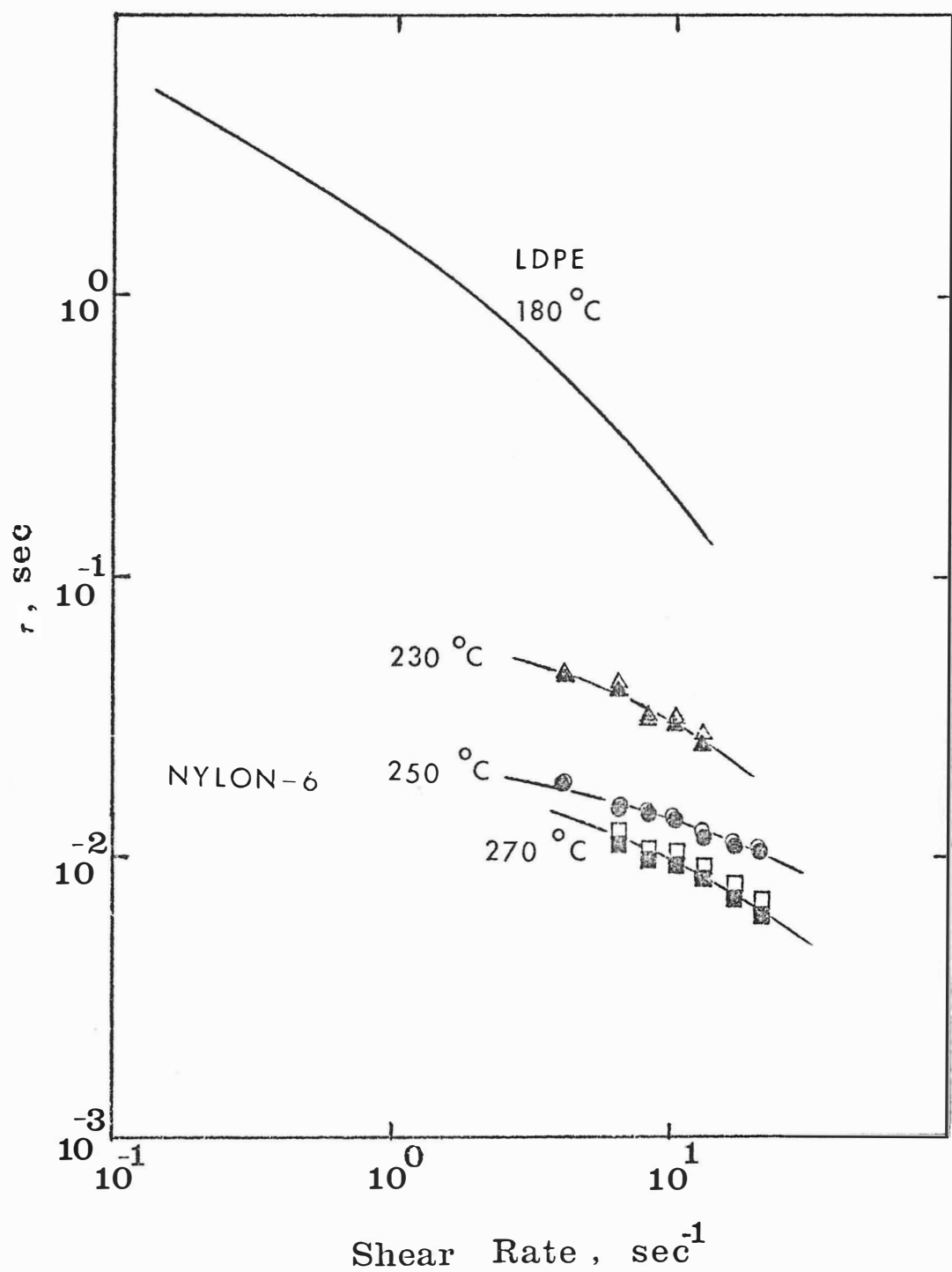


Figure IV-5. Relaxation time of nylon-6 and low density polyethylene melts as a function of shear rate.

which the melt fills the gap.

Combining Equations IV-1 and IV-2, one can obtain true values of ψ_1 as

$$\psi_{1T} = \psi_{1App} \left(\frac{\eta_T}{\eta_{App}} \right)^{2/3} \quad (IV-3)$$

The true relaxation time is now

$$\tau_T = \psi_{1T} / 2\eta_T \quad (IV-4)$$

The "true" values of these parameters were thus calculated using Equations IV-3 and IV-4 and are shown in Figures IV-4 and IV-5 by filled points. For comparison purpose, the results for LDPE are also plotted (37).

Due to flow instability, the radius of the melt within the gap reduced to an effective value. The reduction typically ranged from zero at low shear rates to a maximum value of 8 percent at the highest shear rate used (21 sec^{-1}).

Like viscosity, both ψ_1 and τ decrease with shear rate, though one must be wary of the accuracy. The maximum relaxation time for nylon-6 is 0.03-0.04 seconds at 230°C and 0.011-0.017 seconds at 250°C . If one extrapolates to low shear rates, values of order 0.1 and 0.035 seconds might be obtained. This may be compared with the maximum relaxation time τ_m of nylon-6 obtained by Kotliar (95). He fitted his viscosity-shear rate data of nylon-6 at 250°C to Carreau's model and obtained τ_m of the order of 0.001 to 0.003 sec for samples

having characteristics similar to those used in the present studies. τ_m obtained in the present studies for nylon-6 at 250°C is about 0.03 seconds which is an order of magnitude higher, suggesting that calculations of τ_m based on Carreau model viscosity functions are dubious.

The maximum relaxation time for nylon-6 used in these studies is much smaller than the relaxation time of LDPE (about five seconds). The first normal stress difference coefficient is also about two-three orders of magnitude higher for LDPE than for nylon-6. Thus nylon-6 melt seems to be very Newtonian compared to LDPE.

C. COMPARISON TO THEORIES OF VISCOELASTIC FLUID BEHAVIOR

Comparison of relaxation times for nylon-6 and polyethylene suggests that a rheological model for a Newtonian fluid, Equation II-14 could approximately describe nylon-6 melt. This is indeed the case for the shear viscosity results. The model suggests a viscosity independent of shear rate. The experimental results show that the viscosity is constant in the shear rate range of 0.1 to 20 sec^{-1} . Therefore, in this range, nylon-6 melt could be described by a Newtonian fluid model.

The viscosity drops with shear rate in the range of 20 to 1000 sec^{-1} . The Newtonian fluid model does not predict this. It also does not predict normal stresses. In the present studies, normal stresses are observed at shear rates of 4 sec^{-1} and greater.

In order to describe the behavior of nylon-6 over the entire range of shear rate, more sophisticated models have to be used. Three such models have been attempted in the present studies.

Coleman-Noll Second Order and Third Order Fluids

The second order fluid theory discussed in Chapter II provides second order correction to Newtonian fluid, in that it predicts normal stresses when the fluid is subjected to simple shearing. However, this theory predicts viscosity and first normal stress difference coefficient which are independent of shear rate. As such this theory is still not able to describe the results obtained from the rheogoniometer and the rheometer over the entire range of shear rate. Only the results in the low shear rate region could be described by the second order fluid theory.

The third order fluid described by Equation II-16 predicts both non-Newtonian viscosity and normal stresses.

$$\eta = \omega_1 + 2(\omega_4 - \omega_5)\dot{\gamma}^2 \quad (\text{IV-5})$$

$$\psi_1 = -2\omega_3 = 2\tau\omega_1 \quad (\text{IV-6})$$

This suggests that η begins to vary with shear rate before ψ_1 does. However, our results show that viscosity is almost constant in the range of shear rate where ψ_1 decreases. This is probably again due to flow instability which tends to show a rather rapid decrease in ψ_1 .

White-Metzner Model

The viscosity and the first normal stress difference coefficient for this model are given in Table 1 in Chapter II.

$$\eta = G\tau_{\text{eff}} \quad (\text{IV-7})$$

$$\psi_1 = 2G\tau_{\text{eff}}^2 \quad (\text{IV-8})$$

This agrees reasonably with experiments if we take τ_{eff} as a function of shear rate. This function could, however, only be arbitrary, chosen in such a way as to satisfy experimental results.

The average values of τ obtained from Figure IV-5 and the values of G obtained using Equation (IV-7) are shown in Table 5.

Bogue-White Model

Table I gives the shear viscosity and the first normal stress difference coefficient predicted by the Bogue-White model. The values of τ_m in these equations were taken as $2\bar{\tau}$ since for a box distribution of relaxation spectrum (which was used to derive these equations), τ_m is equal to $2\bar{\tau}$. Figures IV-6 and IV-7 show these functions plotted for different values of the constant "a." The points on these graphs indicate experimental data.

From Figure IV-6, it is clear that the "a" values of 0.18, 0.22 and 0.20 satisfy the viscosity results at 230°C, 250°C and 270°C respectively. We have not tried to fit the model to the viscosity results in the shear rate range of about 6 to 20 sec^{-1} . This is the range where the flow instability was observed, and the results are therefore erroneous.

This is the same range in which the normal stresses are reported. Although we have tried to fit the model to these data in Figure IV-7,

TABLE 5
AVERAGE RELAXATION TIME AND SHEAR MODULUS OF NYLON-6

Temperature °C	$\bar{\tau}$ Seconds	G Dynes/cm ²
230	0.034	2.94×10^5
250	0.014	3.58×10^5
270	0.009	3.66×10^5

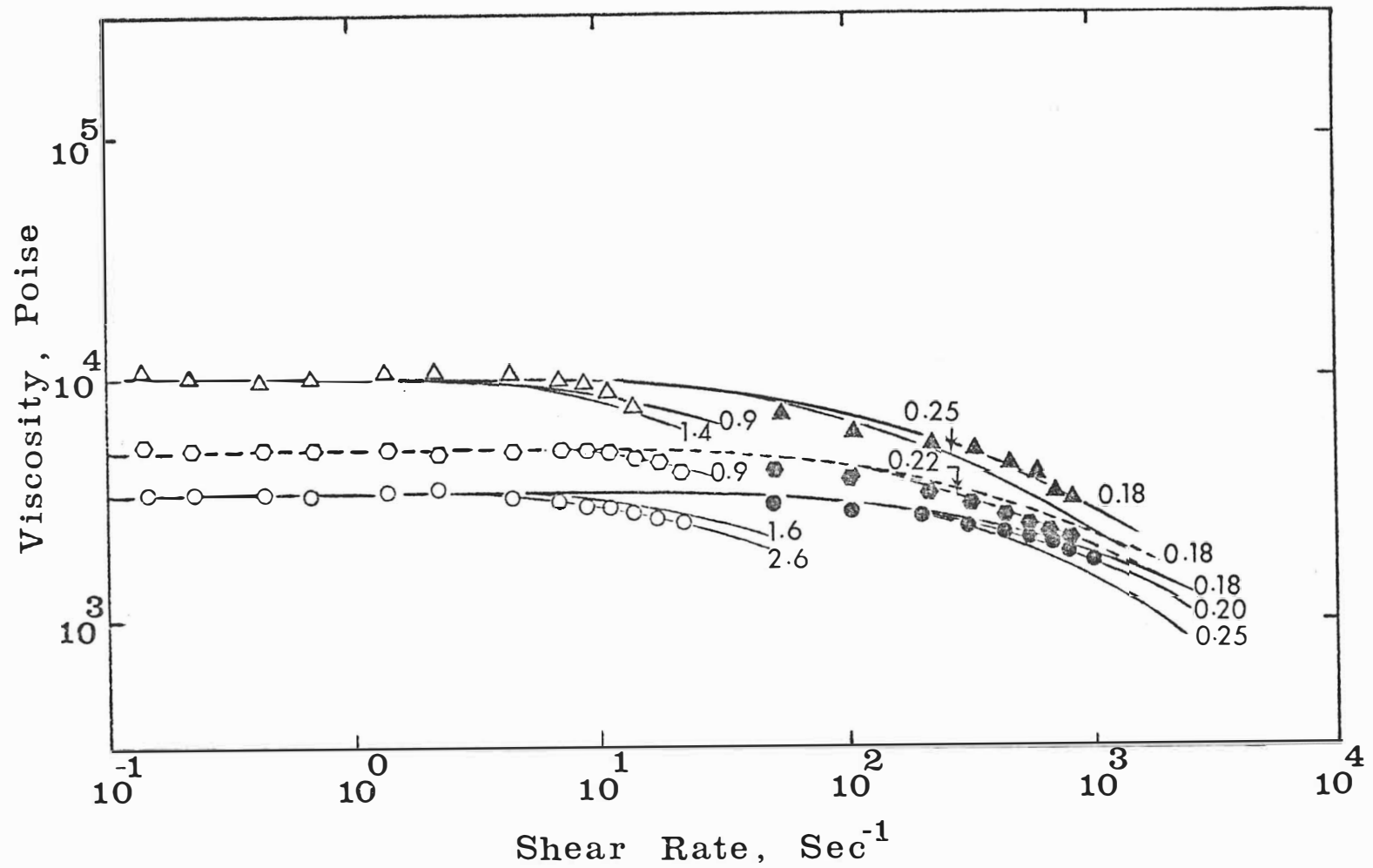


Figure IV-6. Comparison of experimental "shear viscosity-shear rate" relationships with the predictions of Bogue-White model.

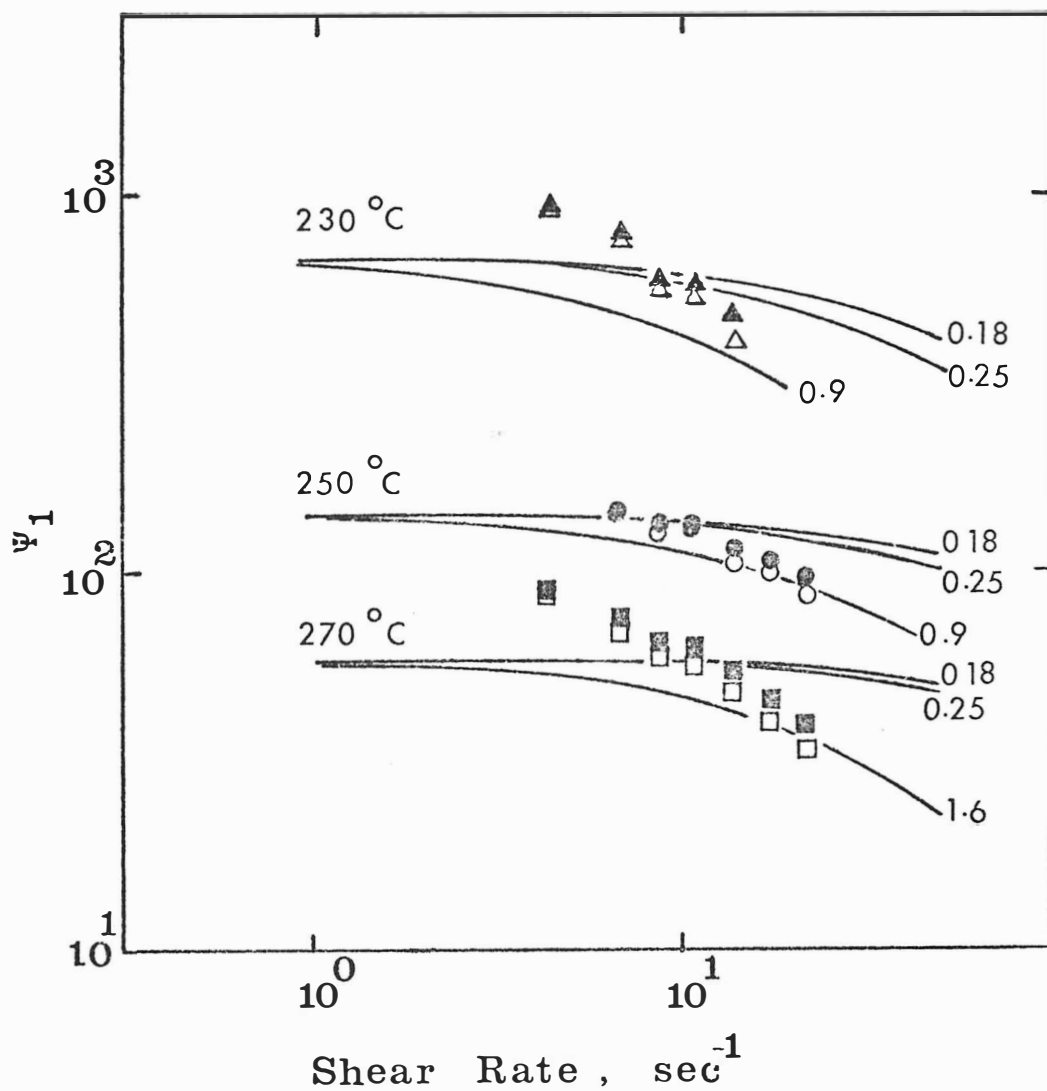


Figure IV-7. Comparison of experimental "first normal stress difference coefficient-shear rate" relationships with the predictions of Bogue-White model.

the attempt is not very successful. There is no qualitative agreement between the experiments and the theory if we use "a" values of 0.18 to 0.22. Using these "a" values, the model suggests nearly constant magnitude of ψ_1 ; but experimentally, ψ_1 is decreasing rapidly. Again, this is due to the flow instability and the thermal degradation of nylon-6 which causes a rapid decrease in ψ_1 .

CHAPTER V

RHEOLOGY OF NON-ISOTHERMAL SPINNING

A. INTRODUCTION

Experiments were carried out on a steady spinline of nylon-6 to study the dynamics and the rheology of non-isothermal spinning. Mono-filaments extruded through a spinneret were allowed to cool down in the ambient air and then taken up on a bobbin. The experimentally obtained profiles of fiber diameter and surface temperature were used along with the fiber tension measured at the take-up device to obtain the stress-deformation-temperature relationship. This relationship was expressed as elongational viscosity as a function of temperature. The methods and the calculations used to obtain it from the fiber diameter, temperature and tension are discussed in this chapter.

The spinning conditions used in these experiments were:

Melt temperature	262°C
Melt pressure	4×10^7 to 6×10^7 dynes/cm ²
Extrusion rate	2.5 gm/min
Take-up speed	100-1000 meters/min
Fiber denier	22.5 - 225

B. DIAMETER, TEMPERATURE AND VELOCITY PROFILES

Results

Fiber diameter and fiber surface temperature are plotted as a

function of distance x from the spinneret in Figures V-1 and V-2 for take-up speed of 100 to 1000 meters/minute. The fiber velocity was calculated point by point from the diameter profile using the continuity equation

$$\frac{\pi d^2}{4} \cdot v \cdot \rho = W = \text{constant} \quad (\text{V-1})$$

The density ρ of the fiber was obtained using the temperature profile of the fiber and the temperature-specific volume relationship for nylon-6 obtained by Inoue (78). This relationship is replotted as temperature-density in Figure V-3. The abrupt change in this curve below about 220°C is due to the change in density caused by crystallization. As will be shown in a later chapter, nylon-6 does not crystallize in the spinline. It remains amorphous in the spinline. Therefore the amorphous density must be used in these calculations. This was obtained by extrapolating the linear portion of the curve to 0°C (shown by a dotted line). The calculated velocity profile is shown in Figure V-4.

Discussion

The diameter profile in Figure V-1 is as expected from earlier studies. The diameter decreases rapidly from its initial value when the polymer is molten. As the fiber cools down and solidifies, the diameter decreases more slowly and finally attains a constant value. The velocity profile similarly increases rapidly in the beginning and finally attains a constant value.

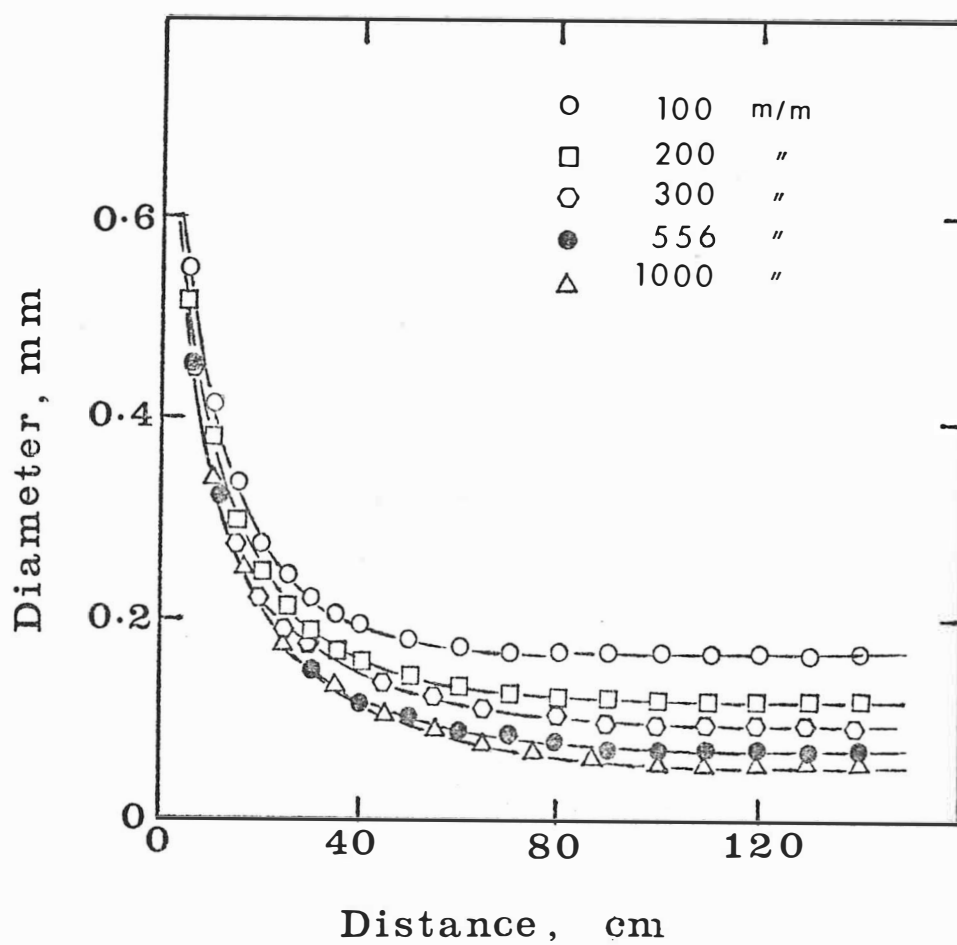


Figure V-1. Fiber diameter as a function of distance from the spinneret in non-isothermal spinning.

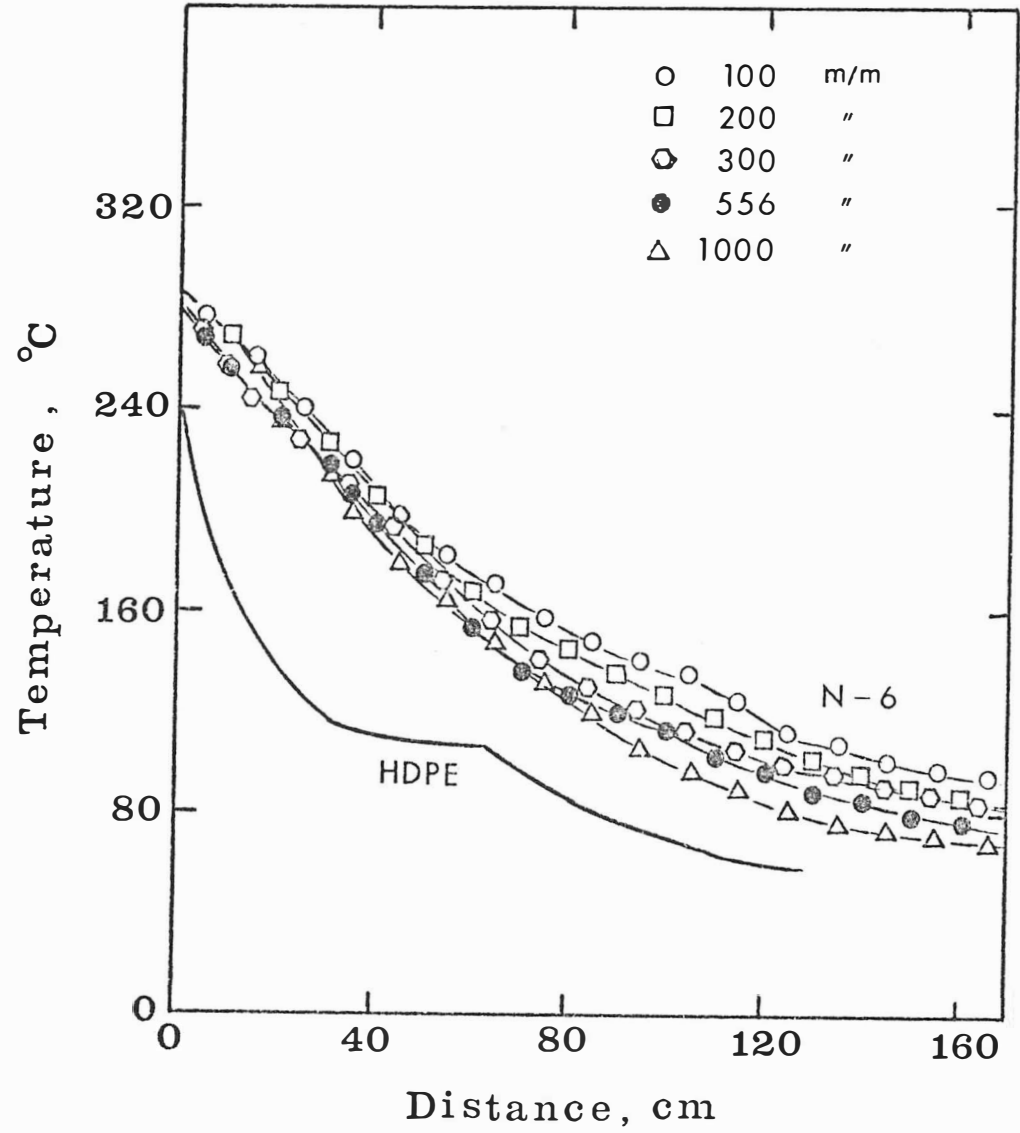


Figure V-2. Fiber surface temperature as a function of distance from the spinneret.

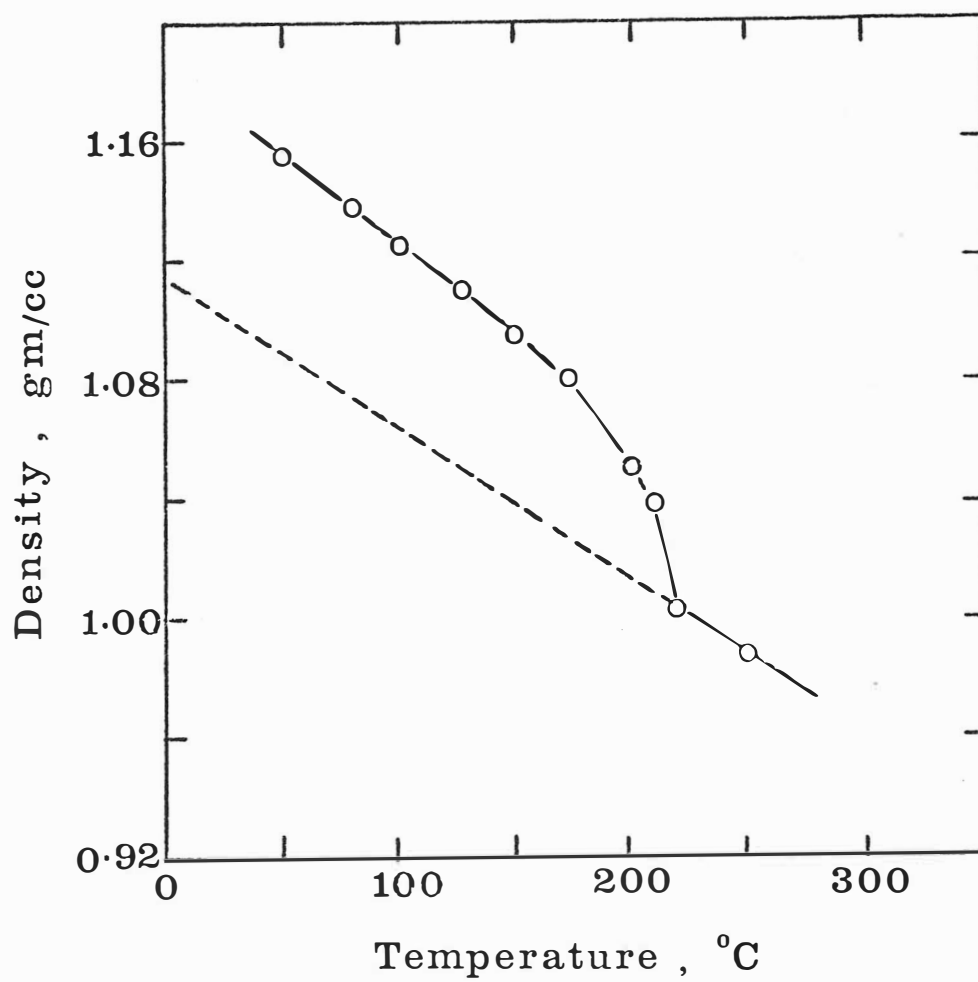


Figure V-3. Density-temperature relationship of nylon-6.

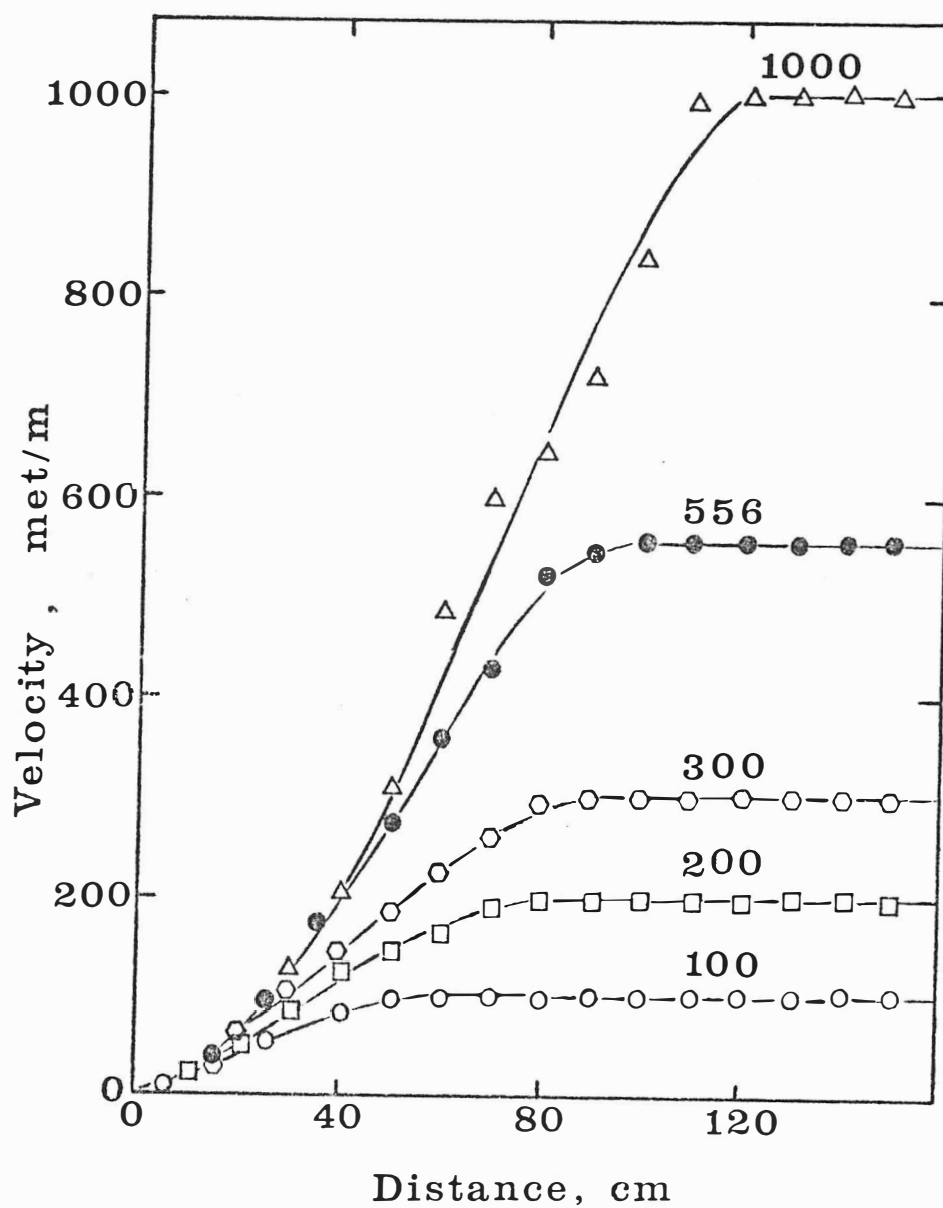


Figure V-4. Fiber velocity as a function of distance from the spinneret in non-isothermal spinning.

The temperature profile in Figure V-2 shows that the fiber cools down rapidly in the beginning, but more slowly as the fiber temperature approaches the ambient temperature. The temperature profiles, when extrapolated to zero distance show that the temperature of the filament at the spinneret exit is about 280-285°C. The melt temperature measured in the spinning block (just before the melt enters the spinneret assembly) is 262°C. It is possible that this difference of 20°C is due to an experimental error in the measurement of fiber temperature very close to the spinneret. In this region the fiber is molten and sticky and the temperature measurement with contact thermocouple becomes very difficult. However, it is possible that the difference arises due to viscous heating of polymer in the spinneret assembly, especially in the filter screen, and the distributor plate plus the capillary.

With increase in the take-up velocity the fiber cools more rapidly. This is in agreement with earlier work (48, 68). It is caused by the increased surface to volume ratio of smaller diameter filaments and also a higher heat transfer coefficient caused by higher linear velocity through the cooling medium.

A typical temperature profile for a high density polyethylene fiber (HDPE) obtained by Dees and Spruiell (48) is also shown in Figure V-2. A significant difference in the temperature profiles of nylon-6 and HDPE is the plateau observed for the latter; but not for the former. This plateau occurs because polyethylene crystallizes on the spinline and the resulting evolution of the heat of crystallization reduces the rate of cooling of the fiber. Dees and Spruiell report 25-40 percent crystallinity of HDPE in the region of the plateau. The

reason nylon-6 does not show such a plateau is either that it has a very low heat of crystallization or it crystallizes to a very low extent on the spinline. The heats of crystallization of 100 percent crystalline nylon-6 and HDPE are 45.6 and 64.8 cal/gm respectively (79). A simple calculation would show that nylon-6 must crystallize to 30-45 percent if it is to produce the same amount of heat as HDPE and show a similar plateau. Since nylon-6 does not show a plateau, it can be concluded that it crystallizes to a very low extent on the spinline. This is not surprising when one notices that the rate of crystallization of nylon-6 is lower than that of HDPE by an order of magnitude or more (e.g., $t_{1/2}$ for isothermal crystallization with 10° undercooling is about 90 minutes for nylon-6 (80) and 9.3 minutes for HDPE (26)). Actually as will be shown in a later chapter, nylon-6 was found to be amorphous in the spinline.

C. SPINLINE FORCE

The variation of spinline take-up force F_{ext} and spinline stress $\sigma (=4 F_{\text{ext}}/\pi d^2)$ with take-up velocity is shown in Figure V-5. Both increase with take-up velocity. The actual force F_{rheo} which acts to deform the descending fiber is not equal to F_{ext} . This could be calculated using Equation II-44 which is discussed in Chapter II.

The methods used for calculation of various force components are given in Appendix A. The aerodynamic drag needs further elaboration.

The drag force per unit length of a fiber of diameter d running at a velocity v can be written from the definition of drag coefficient as

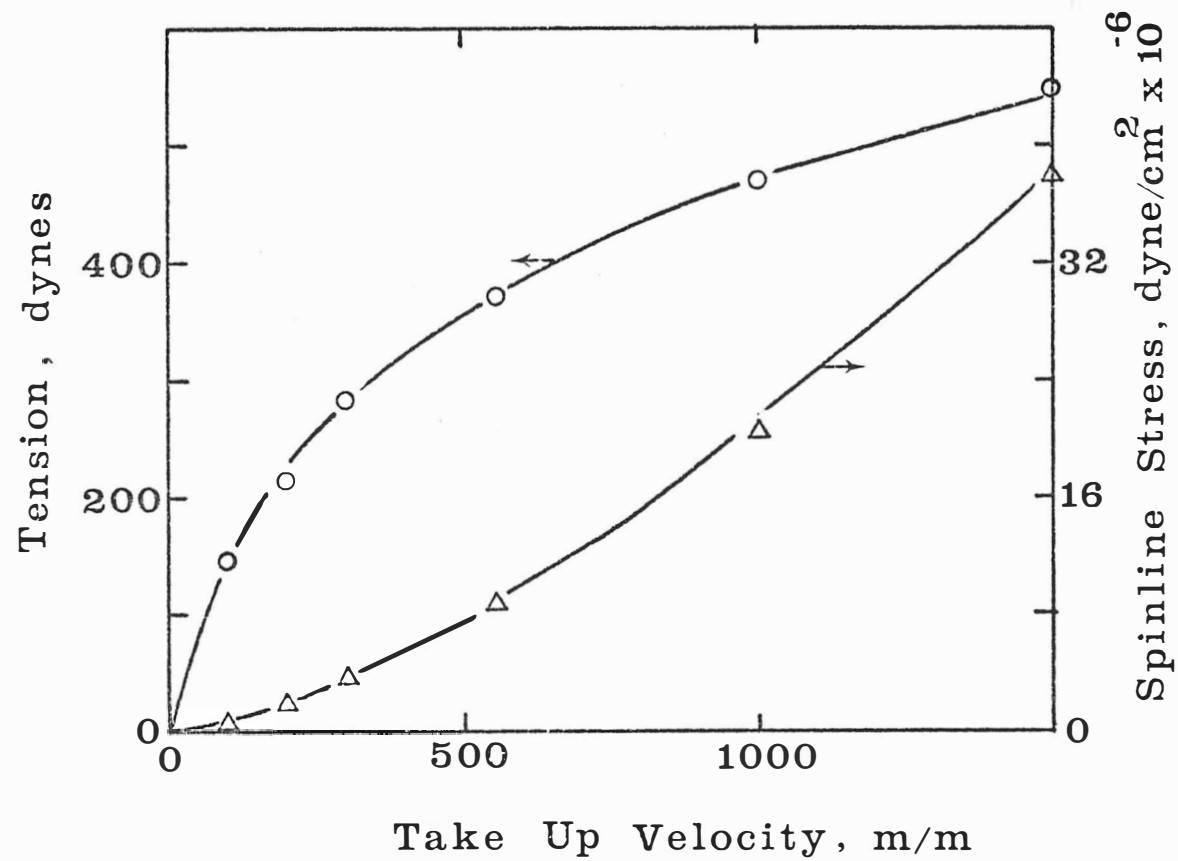


Figure V-5. Variation of spinline tension and spinline stress with take up velocity.

$$\frac{dF_{aero}}{dx} = \frac{\rho_a v^2}{2} \pi d C_f \quad (V-2)$$

where C_f is the drag coefficient which depends on the Reynold's number. ρ_a is the density of the surrounding medium.

As discussed in Chapter II, the C_f -Re relationship has been experimentally obtained by several groups. This is expressed as

$$C_f = m \left(\frac{dv \rho_a}{\mu_a} \right)^{-n} \quad (V-3)$$

The values of m and n obtained by different groups are shown in Table 6 and the C_f -Re relationship has been plotted in Figure V-6. The dotted lines in this figure show the C_f -Re relationship obtained by using Sakiadis' numerical solution of the boundary layer problem for a cylinder running through a stagnant medium. The parameter x/r for fiber spinning is usually about 10^4 to 10^6 . The fiber Reynold's number (based on the diameter) in the present studies lies in the range of about 20 to 60. Figure V-5 shows that in this range, the experimental correlations of Hamana, Matsui and Kato (64) (which we will designate HMK), Sano and Orii (138) (which we will designate S.O.) and Aoki, Suzuki and Ishimoto (5) (which we will designate ASI) give almost equal values of drag coefficient. The Andrews' experiments (4) show very high drag whereas the Sakiadis' analysis shows a lower drag.

In order to see what effects these different C_f -Re relationships have on the rheological force-spline deformation relationship, the aerodynamic drag was calculated using all these expressions. The expression due to Andrews was omitted because it gave ridiculously high

TABLE 6
CONSTANTS m AND n IN EQUATION V-3 OBTAINED BY VARIOUS
RESEARCH GROUPS

Research Group	m	n
Andrews (4)	1.3	0.61
Hamana, et al (64)	0.37	0.61
Sano and Orii (138)	0.68	0.8
Aoki, et al. (5)	0.18	0.44

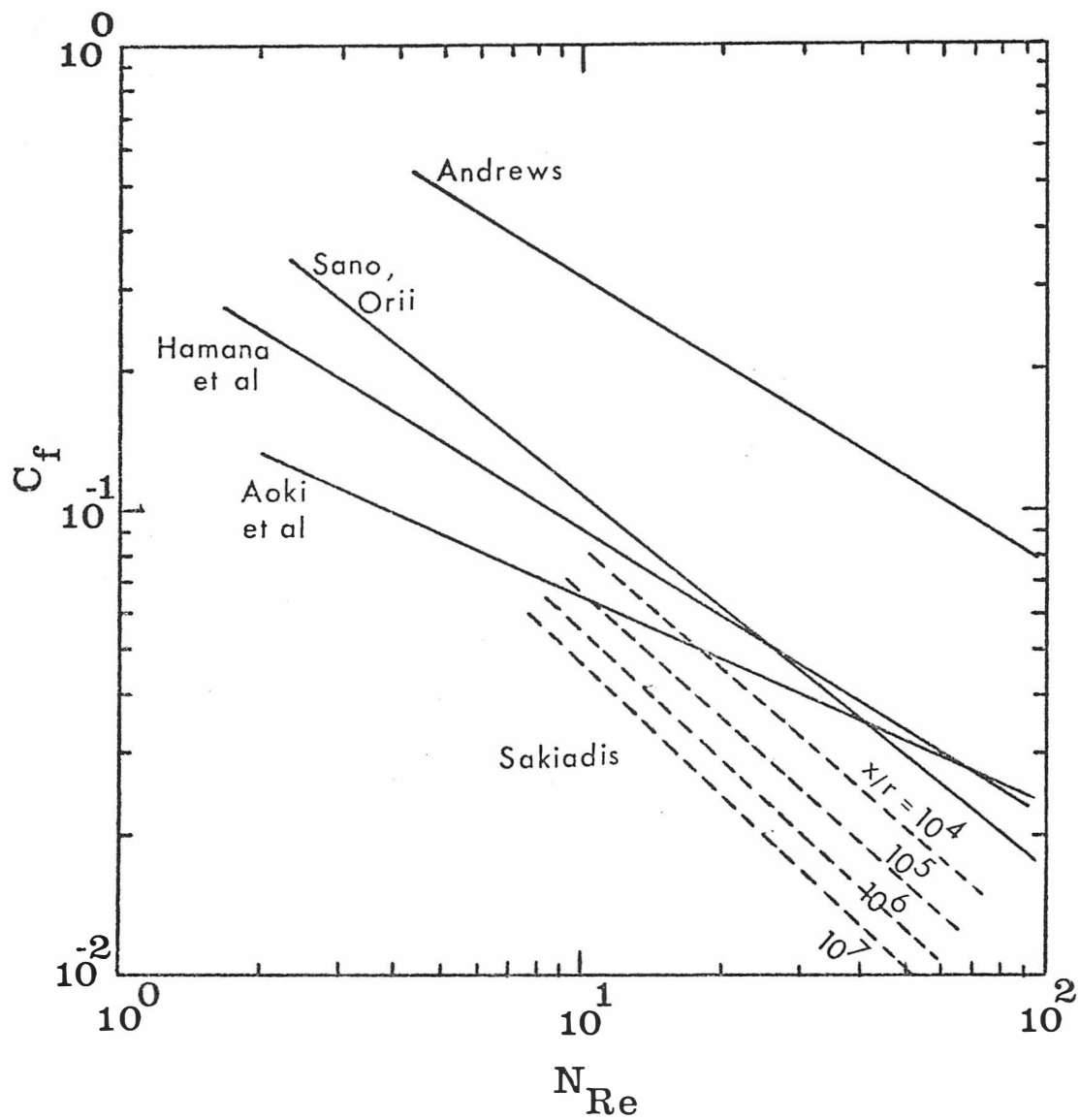


Figure V-6. Friction factor coefficient as a function of Reynolds number for a fiber moving through a stagnant medium.

magnitudes of drag force. As it is evident from Figure V-6, the drag forces calculated by using different experimental correlations (HMK, SO and ASI) are almost equal (within 5 to 10 percent of each other) but are consistent in being 200-250 percent higher than the drag force predicted by the Sakiadis analysis.

Let us try to rationalize this difference. As shown in Appendix A, the Sakiadis analysis was used with average values of velocity and diameter of fiber. However, most of the drag is produced by the solidified fiber having constant final diameter and running at the maximum velocity (equal to the take-up velocity). Therefore, the calculations based on the average values are probably underestimated. When the calculations were made based on the maximum velocity and the final constant diameter, rather than the average values, an increase in the drag force of about 17-20 percent was obtained. Thus the use of average values of diameter and velocity contributed only slightly to the difference of 200-250 percent cited in the preceding paragraph.

It seems that this difference arises because the turbulence in the boundary layer at high take-up velocity is not properly considered in the Sakiadis analysis. The experimental correlations were also based on the measurements of tension in the fiber. These measurements are not always very accurate and they could introduce some errors.

The rheological force was calculated using Equation II-44 and the calculated values of various force components. At low take-up velocity, there was no significant difference in the magnitudes of F_{rheo} obtained by using different C_f -Re relationships for calculations of frictional drag. However, at high take-up velocities, F_{rheo} obtained by using

Sakiadis drag theory was higher by as much as 50-100 percent (for 1000 m/min take-up velocity) than F_{rheo} obtained by using various experimental C_f -Re correlations.

In Figures V-7 and V-8 various force components have been shown at take-up velocities of 100 m/min and 1000 m/min respectively. The dashed lines show the drag force and the rheological force based on experimental C_f -Re relationship of Hamana, et al. The solid lines are based on the calculations using Sakiadis theoretical analysis. It is clear from Figure V-7 that the inertia and the aerodynamic drag are quite negligible at low take-up velocity but become significant at higher velocity. The reverse is true for the gravity force. The assumption of constant rheological force often made in the study of rheology of spinning is quite valid at low take-up velocities but is not so good at higher take-up velocities. At high take-up velocities, F_{rheo} increases along the spinline.

D. ELONGATIONAL VISCOSITY

The elongational viscosity was calculated point by point using

$$\chi(T) = \frac{F_{rheo}/A}{dv/dx} \quad (V-4)$$

where dv/dx is the elongation rate obtained from the velocity profile. Local χ is plotted against the fiber temperature in Figures V-9 and V-10. Experimental C_f -Re correlations of Hamana, et al. was used to obtain χ which is plotted in Figure V-9 and Sakiadis analysis was used for Figure V-10.

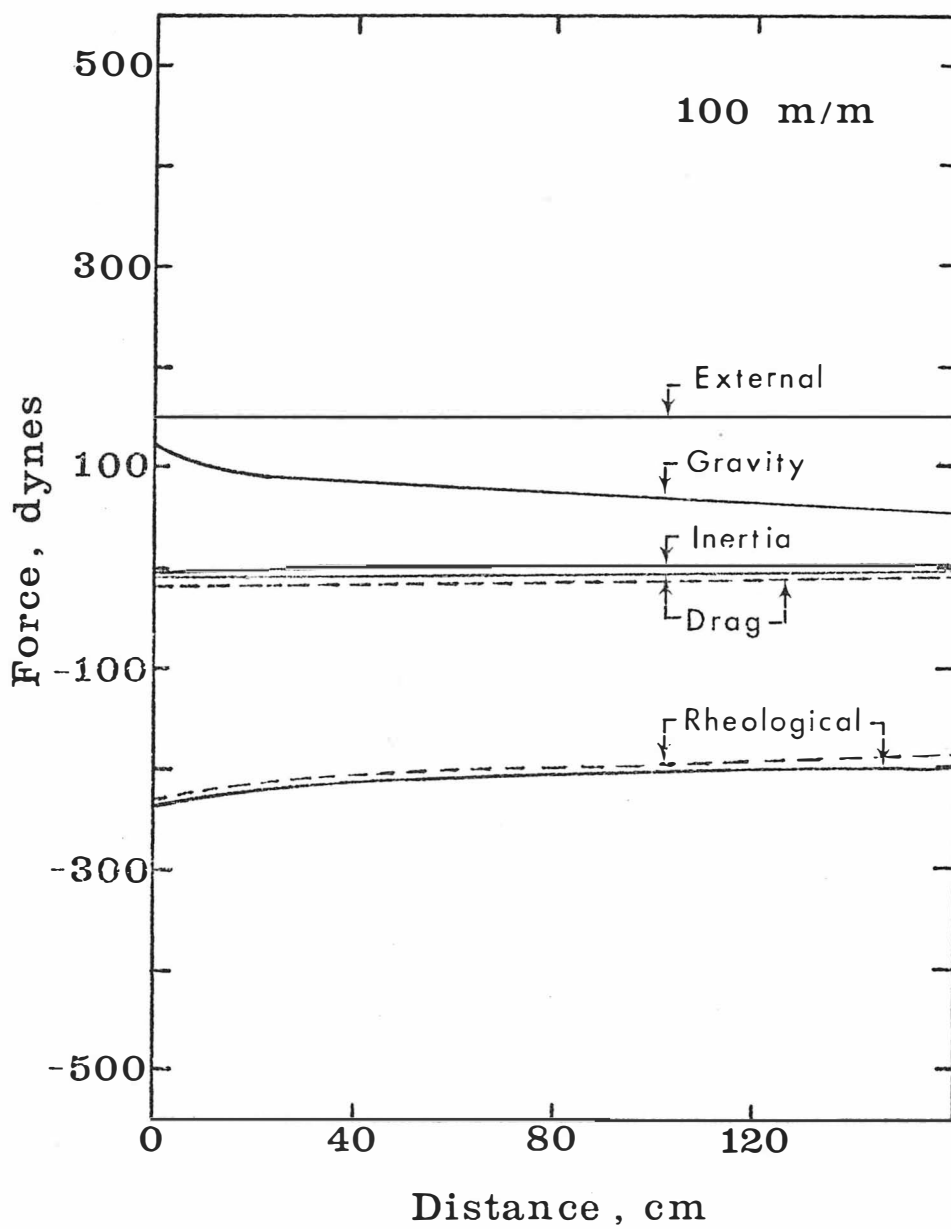


Figure V-7. Force distribution within a spinline, 100 m/min.

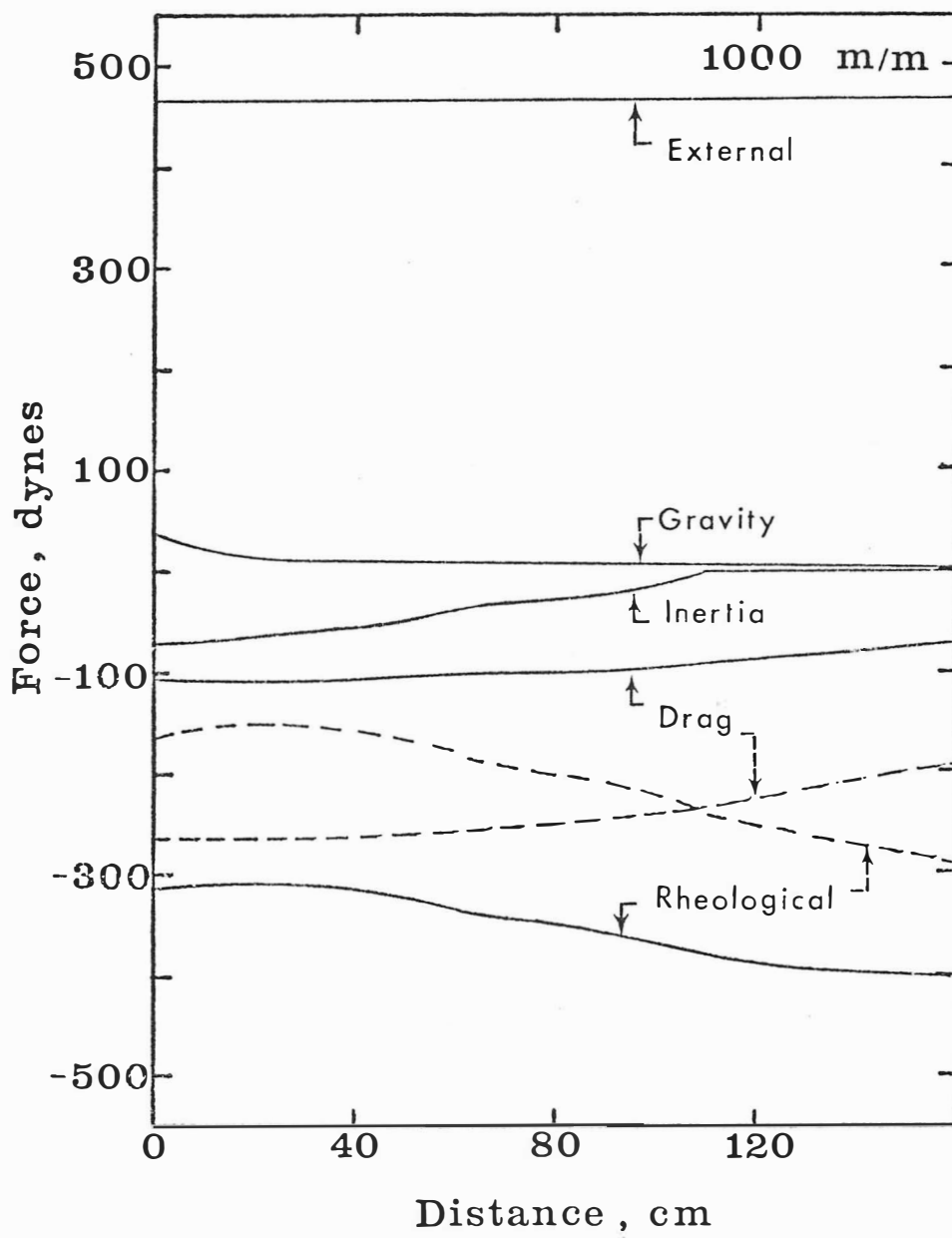


Figure V-8. Force distribution within a spinline, 1000 m/min.

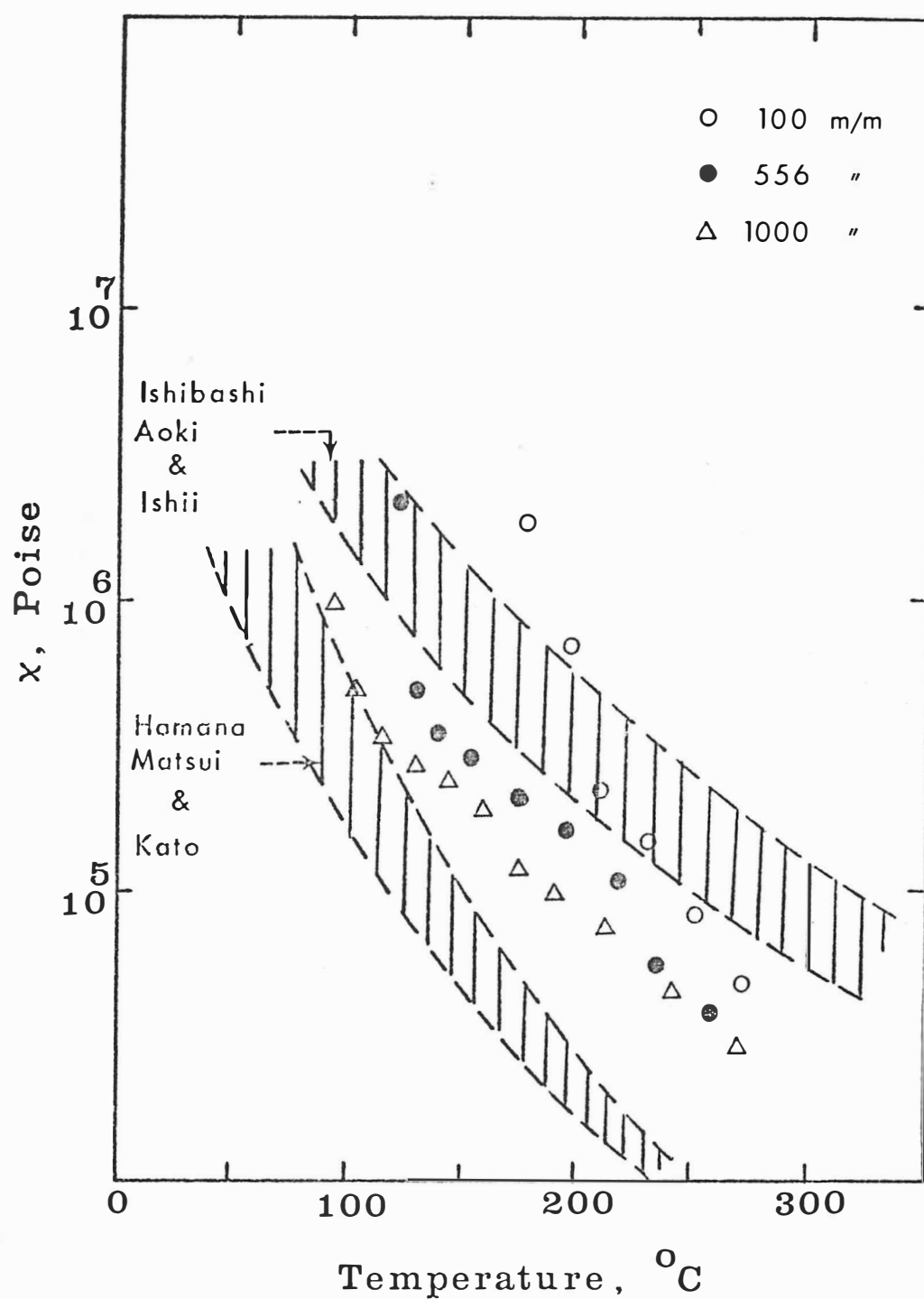


Figure V-9. Elongational viscosity-temperature relationship for nylon-6 fibers. Calculations are based on C_f -Re relationship of Hamana, Matsui and Kato (64).

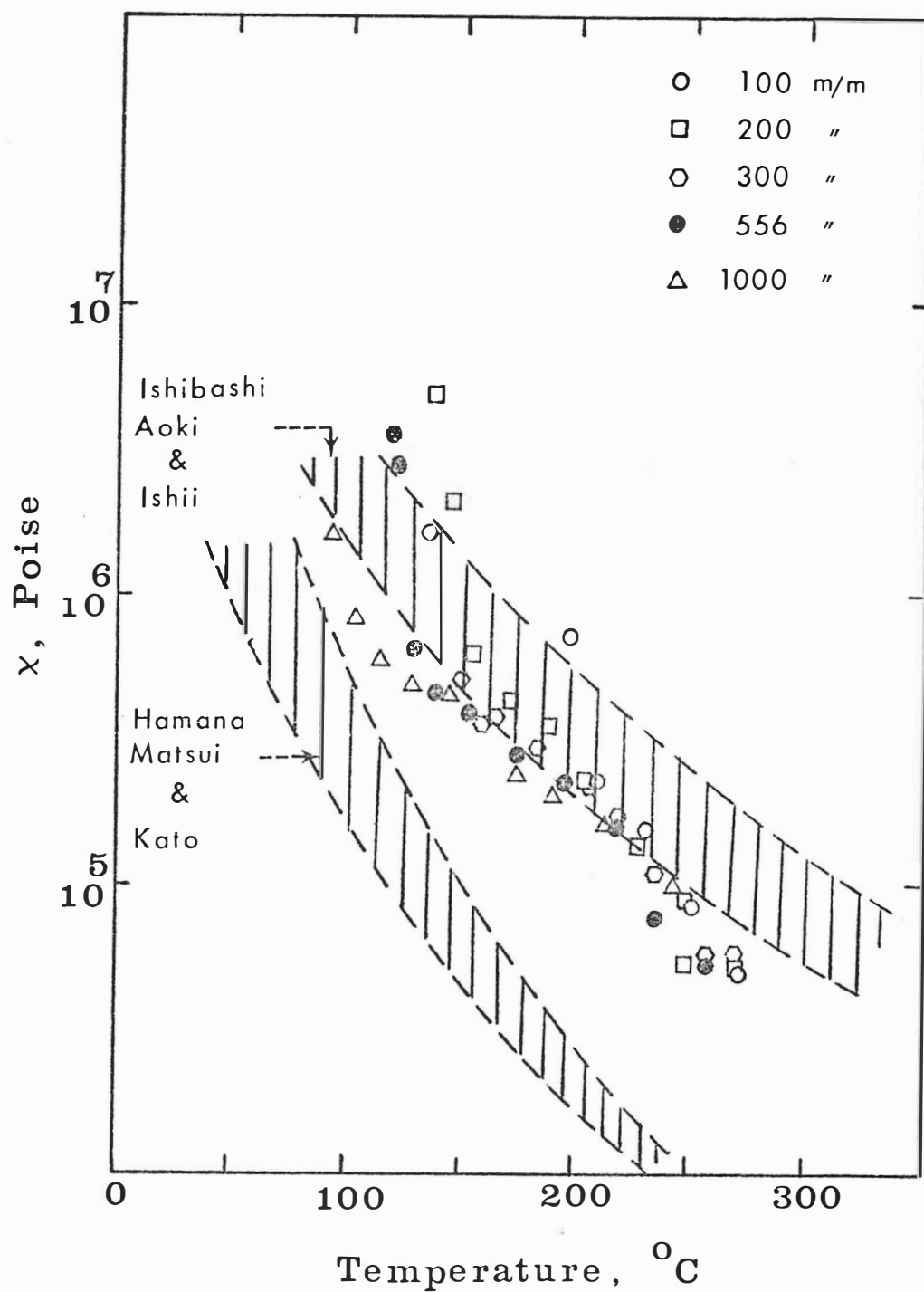


Figure V-10. Elongational viscosity-temperature relationship for nylon-6 fibers. Calculations are based on Sakiadis analysis of friction factor coefficient (135).

χ values obtained at different take-up velocities are quite close to each other at high temperatures but spread apart at lower temperatures. Moreover, this spread is much greater in Figure V-9 where experimental C_f -Re relationship of Hamana, et al was used. They predict high F_{aero} and also high difference in F_{aero} at different take-up velocities. This results in wide difference in F_{rheo} and consequently in χ .

In Figure V-10, χ -T relationship obtained by Ishibashi, et al. (81) and Hamana, et al. (65) are also plotted. The latter authors used the HMK correlation for obtaining air drag and observed a spread in data similar to that in Figure V-9, the reasons for which are discussed in the preceding paragraph. Surprisingly, Ishibashi, et al. obtained a similar spread too, even though they used Sakiadis analysis to calculate air drag. It seems that all these experiments depend very much on the measured take-up tension and the methods used for these measurements are not very accurate.

The χ values obtained in the present studies are quite similar to those of Ishibashi, et al. but much larger than those of Hamana, et al.

This difference is due to the difference in molecular weights of nylon-6 used in these studies. The M_n value of nylon-6 used in the present experiments is 23,000. Ishibashi, et al report M_n for the nylon-6 they used (measured after extrusion) to be 19,000. Hamana, et al. report the viscosity average molecular weight of their polymer as 16,000. If their $[\eta]$ - M relationship was based on narrow fractions,

then $M_\eta / M_n \approx 1.8$ and their $M_n < 10,000$. These figures are sufficient to explain the results shown in Figure V-10.

CHAPTER VI

RHEOLOGY OF ISOTHERMAL SPINNING

A. RESULTS

Fibers were spun at 200, 300 and 556 meters/minute take-up velocities through an isothermal chamber maintained at $270 \pm 2^\circ\text{C}$. Measurements were made of fiber diameter and tension. The fiber velocity and the rheological force were evaluated in the same manner as for non-isothermal spinning. Figure VI-1 and Figure VI-2 show the diameter and the velocity profiles. A slight die-swell is observed before the diameter starts decreasing.

The elongational viscosity was calculated in the same manner as for non-isothermal spinning. Figure VI-3 shows the elongational viscosity plotted as a function of elongation rate. The elongation rate was obtained from the velocity profile. On the same plot are drawn the curves for the shear viscosity η and 3η , obtained from the rheogoniometer experiments, plotted as functions of shear rate. The elongational viscosity lies in the range of 4×10^4 to 6×10^4 poise and it increases with the elongation rate.

B. DISCUSSION

If the nylon-6 melt was strictly a Newtonian fluid, its elongational viscosity would be equal to 3η . This is shown in Figure VII-3 by the $3\eta-\dot{\gamma}$ curve. The χ values obtained from the spinning experiments

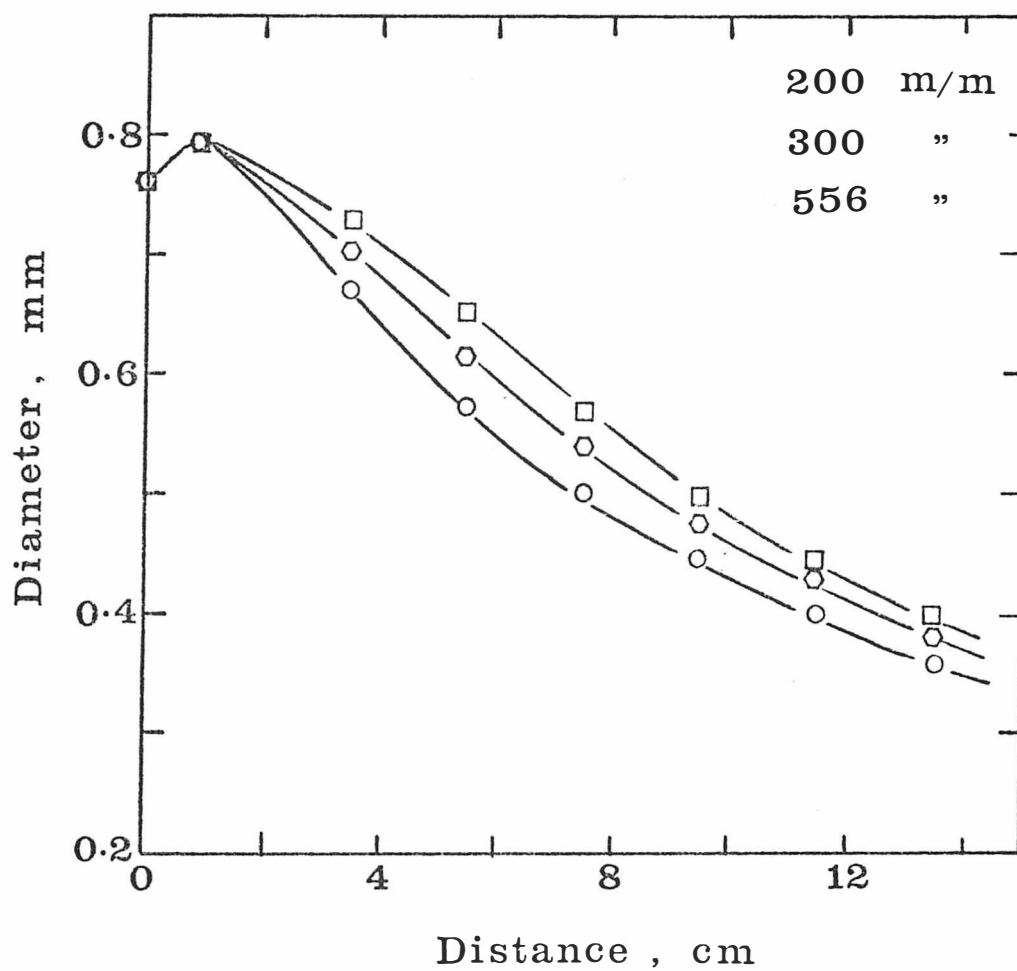


Figure VI-1. Fiber diameter as a function of distance from the spinneret in isothermal spinning.

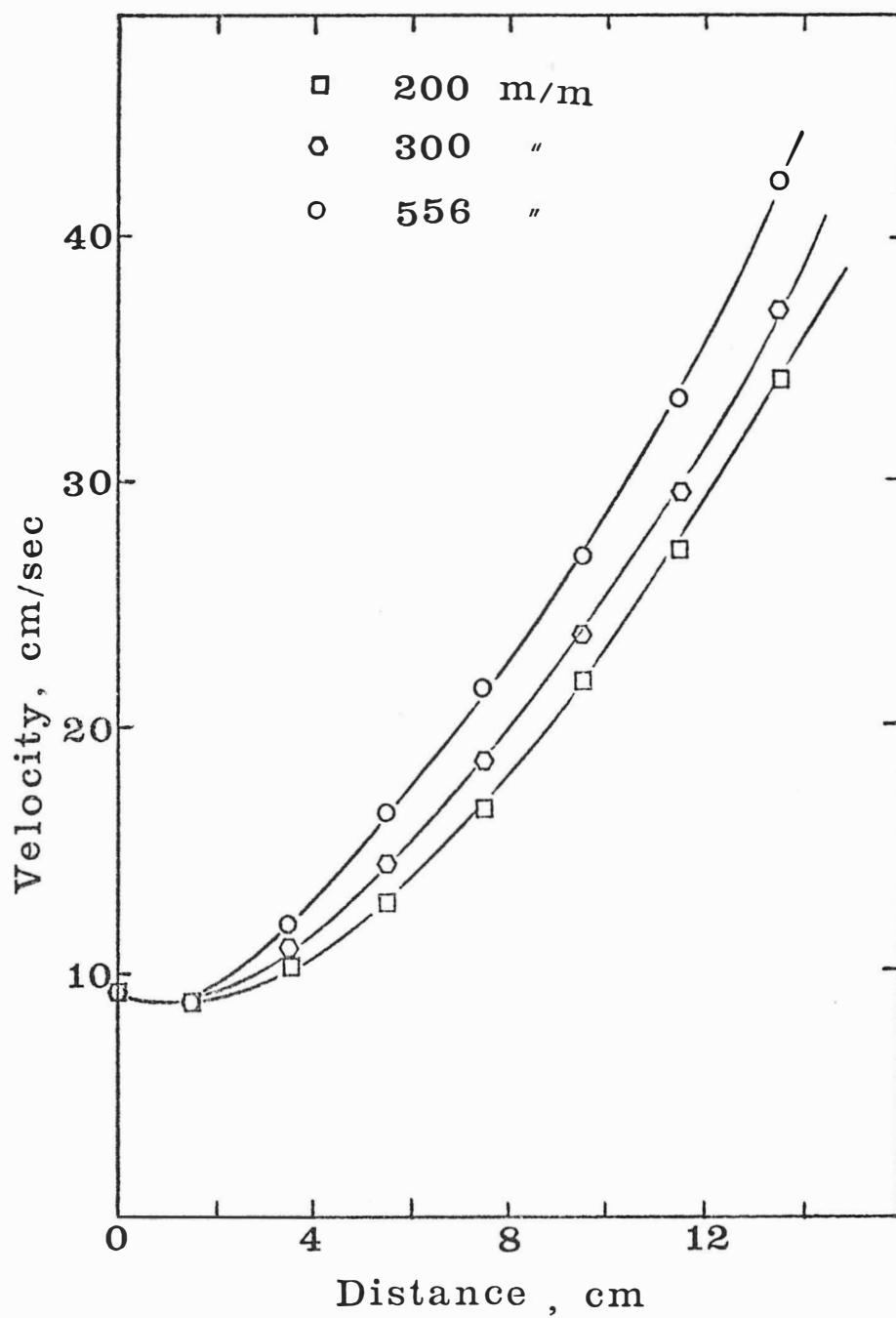


Figure VI-2. Fiber velocity as a function of distance from the spinneret in isothermal spinning.

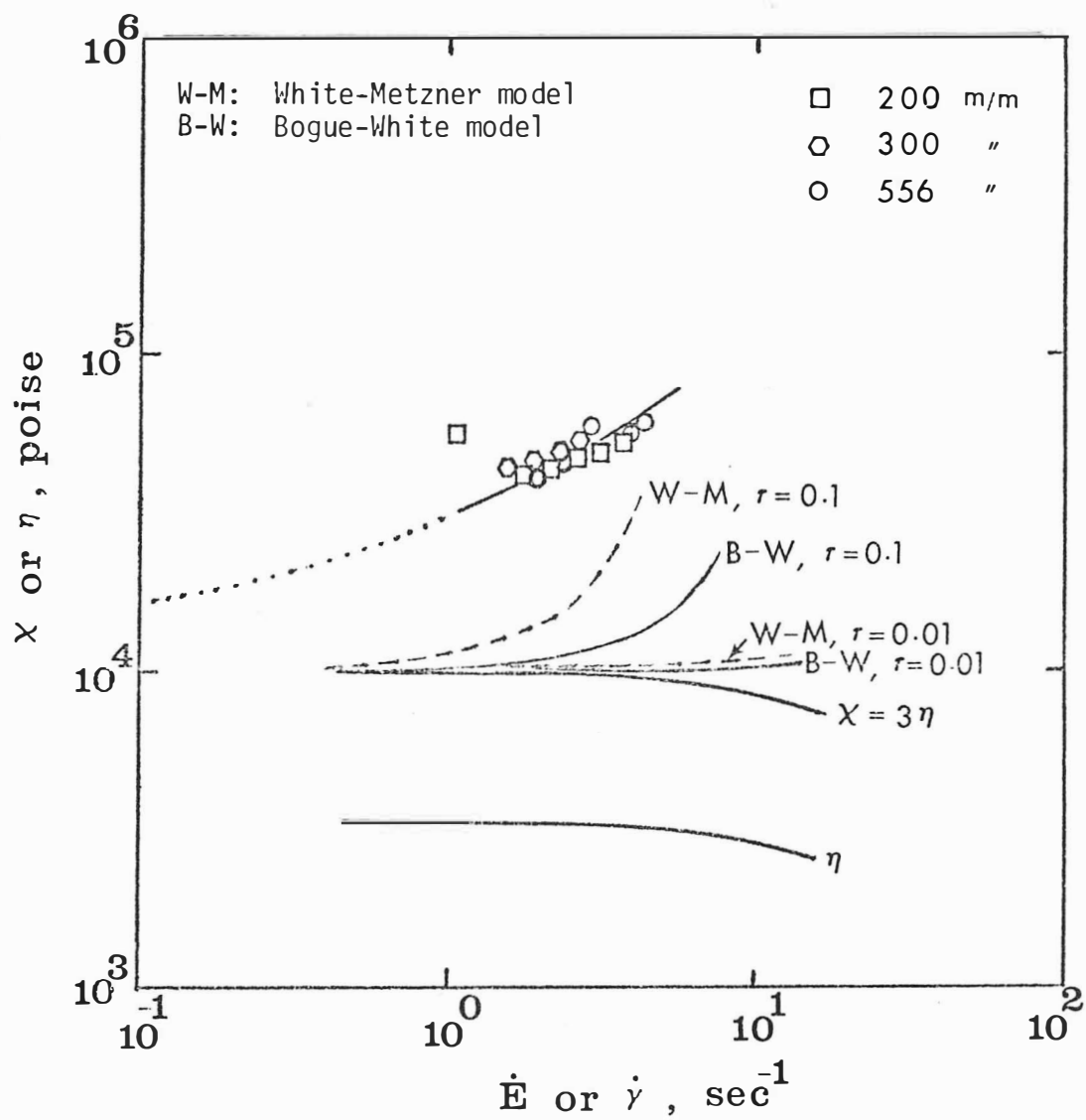


Figure VI-3. Experimental and theoretical elongational viscosity as a function of elongation rate.

are about 15 times higher than the shear viscosity η and five times higher than the Newtonian prediction, 3η , and they also increase with the elongation rate. If one extrapolates the spinning data to low elongation rates (as shown by the dotted line), it is possible to meet the $3\eta-\dot{\gamma}$ curve.

It would appear that the nylon-6 melt is behaving more like a viscoelastic fluid in the spinning experiments. The high magnitudes of χ and the viscoelastic behavior of nylon-6 in spinning are quite surprising in view of the shear experiments which undoubtedly showed a more Newtonian fluid-like behavior.

It is possible to estimate χ/η ratio for nylon-6 melts from the earlier studies of Hamana, Matsui and Kato (65) and Ishibashi, Aoki and Ishii (81). These authors obtained non-isothermal $\chi(T)$ data. They did not report the shear viscosity η of the melts but reported the molecular weights. Using these molecular weight figures and the $\eta - M_n$ relationship for nylon-6 obtained by Pezzin and Gechele (128), one can estimate the shear viscosity η . Combining this with the $\chi(T)$ measurements, we estimated χ/η ratio for their polymers. The ratio was about eight for lower molecular weight polymer of Hamana, et al, and was no less than 20 for a high molecular weight sample of Ishibashi, et al. Moreover, in a private communication, McKoy of Monsanto reported that this ratio was 15 for nylon-66 melts. This would seem to confirm the high values of χ that we observed in our experiments.

The elongational viscosity approach used in our studies (i.e., $\chi = \frac{F/A}{dv/dx}$) is perhaps questionable because the elongation rate in our experiments is changing. In our experiments, the residence time of the melt in the isothermal chamber is about 0.6 seconds. $\tau_m (=2\bar{\tau})$

at 270°C from Chapter IV, is about 0.02 seconds. This leads to an apparent Deborah number (19) of the process

$$N_{\text{Deb}} = \frac{\tau_m}{t_{\text{res}}} \quad (\text{VI-1})$$

of 0.034 which is small. However, the variation in dv/dx along the spin-line makes it questionable whether such a choice of average residence time which gives a global Deborah number is appropriate. From the velocity profile in Figure VI-2, it seems that dv/dx would tend to become constant further away from the spinneret. (Perhaps experiments with a longer isothermal chamber would establish this.) Deborah number based on this constant dv/dx is probably more appropriate

$$N_{\text{Deb}} = \tau_m \cdot \frac{dv}{dx} \quad (\text{VI-2})$$

This leads to N_{Deb} values of order 0.08 or higher and suggests that viscoelasticity needs to be considered.

As the first approximation, it was attempted to use the White-Metzner model and the Bogue-White model (with a box distribution of relaxation times), along with the material parameters obtained in the shear experiments to predict the elongational viscosity. In such a procedure we neglect the transient viscoelastic response. In Figure VI-3 dashed lines show predictions of the White-Metzner model and the solid lines show the predictions of the Bogue-White model for two different relaxation times, 0.01 seconds and 0.1 seconds. The relaxation time

obtained in the shear experiments at 270°C was approximately 0.01 seconds. It is seen that the predicted values of χ are close to 3η and are quite different from the experimental χ .

The analysis of Denn, Petrie and Avenas (49) which is a more rigorous solution of the White-Metzner model was also used to predict the relaxation time from the spinning data. The Newtonian asymptote, $\alpha \rightarrow 0$, and the asymptote of high imposed stresses compared to the modulus, $\epsilon/\alpha \rightarrow 0$, as well as the numerical solution were used to obtain the relaxation time. In using this analysis, Denn, et al's v term was taken to be zero and the initial boundary conditions were taken as those at the point of maximum die-swell. Table 7 shows the values of relaxation times obtained for different cases.

The first two columns were obtained by using the expressions for the relaxation time derived by Denn, Petrie and Avenas. These are written after simplification as

$$\alpha \rightarrow 0, \quad \tau = \frac{x}{v_x} \left(\frac{1}{\ln \frac{v_x}{v_0}} - \frac{3\eta Q}{F \cdot x} \right)^{1/2} \quad (\text{VI-3})$$

$$\frac{\epsilon}{\alpha} \rightarrow 0, \quad \tau = \frac{x}{v_x - v_0} \left[1 - \frac{3\eta Q}{2Fx} \left\{ \ln \frac{v_x}{v_0} + \frac{1}{2} \left(1 - \frac{v_0^2}{v_x^2} \right) \right\} \right] \quad (\text{VI-4})$$

The last column was obtained by fitting the experimental velocity profiles with the profiles obtained by numerically solving the momentum and the continuity equations simultaneously. The third order Runge-Kutta method was used for this purpose. Figure VI-4 shows an example of such velocity

TABLE 7

RELAXATION TIME CALCULATED USING THEORY OF
DENN, PETRIE AND AVENAS

Take-Up Velocity m/min	Relaxation Time, Sec		
	$\alpha \rightarrow 0$	$\frac{\varepsilon}{\alpha} \rightarrow 0$	Numerical Solution
200	0.378	0.694	0.45 to 0.60
300	0.309	0.520	0.40 to 0.50
556	0.245	0.390	0.35 to 0.45

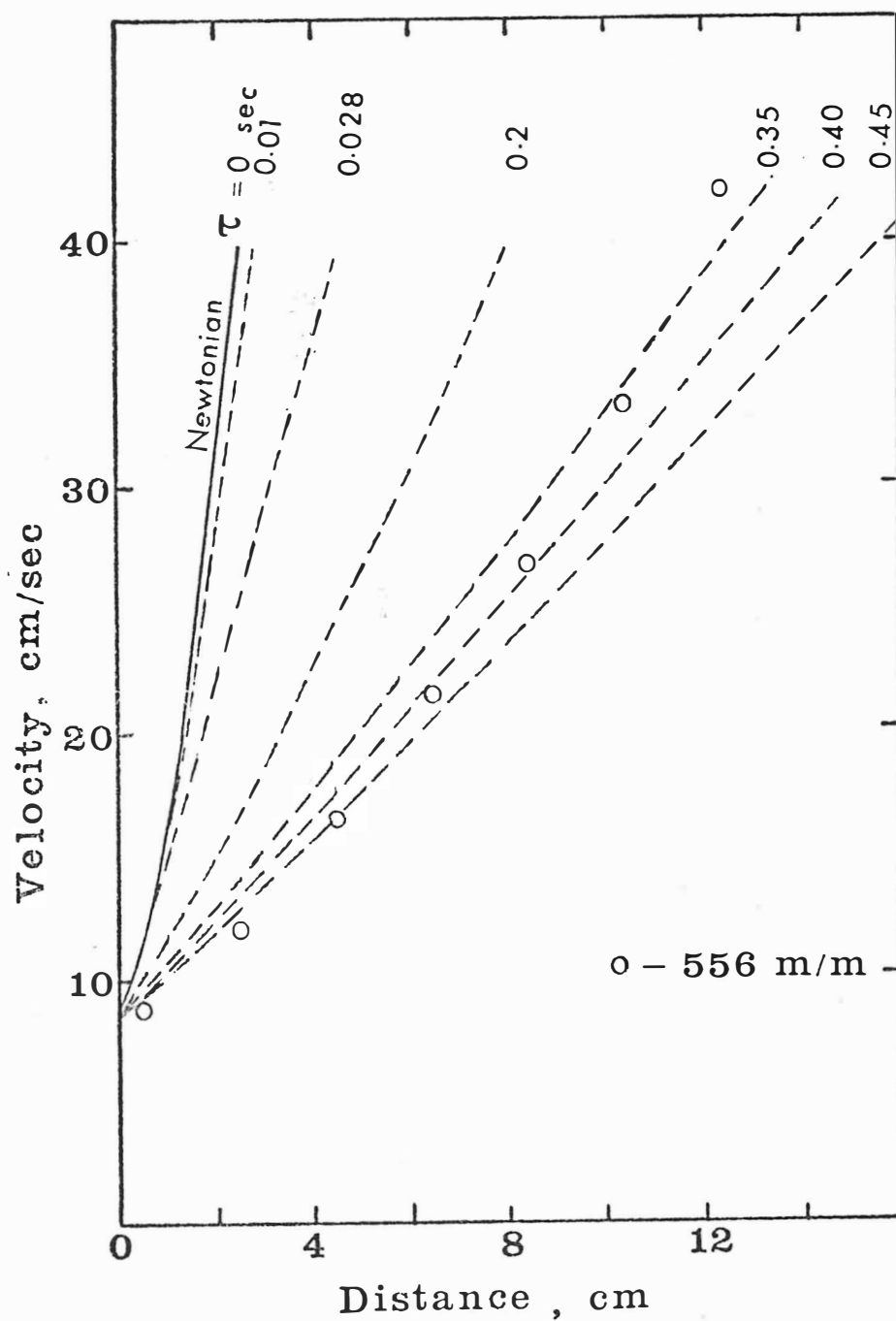


Figure VI-4. Comparison of experimental fiber velocity profile with the predicted profiles obtained by using Denn, Petrie and Avenas theory (49).

profiles for different values of relaxation times for a take-up velocity of 556 m/m. The velocity profile predicted by using $\bar{\tau} = 0.01$ seconds (this is the relaxation time determined from the shear experiments) is seen to be very close to the Newtonian prediction ($\bar{\tau} = 0$).

Table 5 shows that the relaxation time obtained from the spinning data is more than an order of magnitude higher compared to that obtained from shear experiments.

The comparison made so far of the predictions of various viscoelastic theories with the results of spinning experiments shows a wide disagreement. The material appears to be much more viscoelastic.

At first, it was thought that the temperature of the fiber in the isothermal chamber might not be really the same as the chamber temperature itself. This would give material properties different from what they are thought to be. However, allowing the fiber temperature to deviate as widely as 20°C from the chamber temperature would not reduce the difference between χ and η appreciably or increase $\bar{\tau}$ significantly.

It is attractive to think [in line with the conclusion of Chen, et al. (38)] that the discrepancy was due to inadequate framing of melt prehistory. However, for a relatively inelastic fluid like nylon-6 melt, the prehistory should be rather insignificant.

In conclusion, it may be said that the nylon-6 melt responds in the spinline as if it has a much higher elongational viscosity and memory than would be expected, based on a rheogoniometric shear data. None of the rheological models considered here are able to represent the behavior of molten nylon-6. Perhaps the only consistent explanation might be that the melt has a wide relaxation spectrum and $H(\tau)$ decreases

very slowly at large τ so that the ratio $\tau_m/\bar{\tau}$ is large. It is also possible that we might have some error in our $\bar{\tau}$ values because of the flow instability and degradation.

CHAPTER VII

STRUCTURE DEVELOPMENT AND MORPHOLOGY

A. ON-LINE STRUCTURE DEVELOPMENT

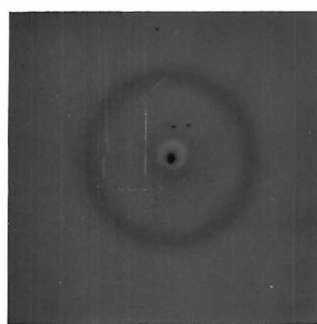
Results

Wide angle x-ray diffraction patterns of a portion of a running spinline about 160 cm below the spinneret were taken at different take-up velocities. The exposure time ranged from three to five hours depending on the diameter of the spinline. Diffraction patterns were taken for filaments spun in air of about 65 percent relative humidity as well as in the constant humidity chamber with 100 percent R.H. Fiber temperature at the point where x-ray measurements are carried out was about 80-90°C. This is well below 140°C which is the temperature of maximum rate of crystallization (101). Figures VII-1 and VII-2 show these patterns for two different take-up velocities. All the patterns consist of single diffuse halos whose average d-spacings correspond to about 4.23 to 4.33Å°.

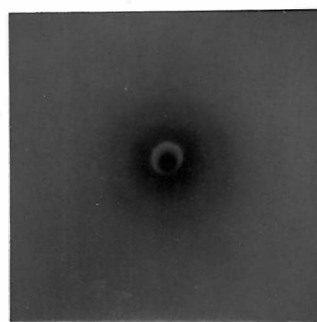
The birefringence of the running filaments was also measured at different positions along the spinline for take-up velocities ranging from 100 m/min to 1000 m/min. Figure VII-3 shows these birefringence profiles.

Discussion

Roldan and Kaufman (132) showed that the d-spacings of 4.16Å° to 4.3Å° of nylon-6 diffraction pattern is obtained from quenched

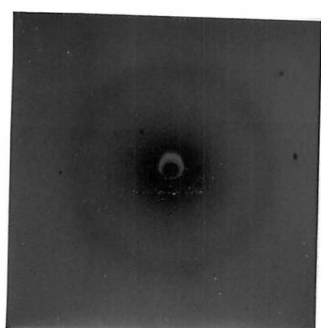


(A) 100 m/min

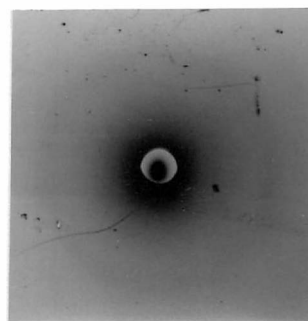


(B) 1000 m/min

Figure VII-1. On line WAXS patterns of nylon-6 spinline. Fiber spun in 65 percent relative humidity environment.



(A) 200 m/min



(B) 556 m/min

Figure VII-2. On line WAXS patterns of nylon-6 spinline. Fiber spun in 100 percent relative humidity environment.

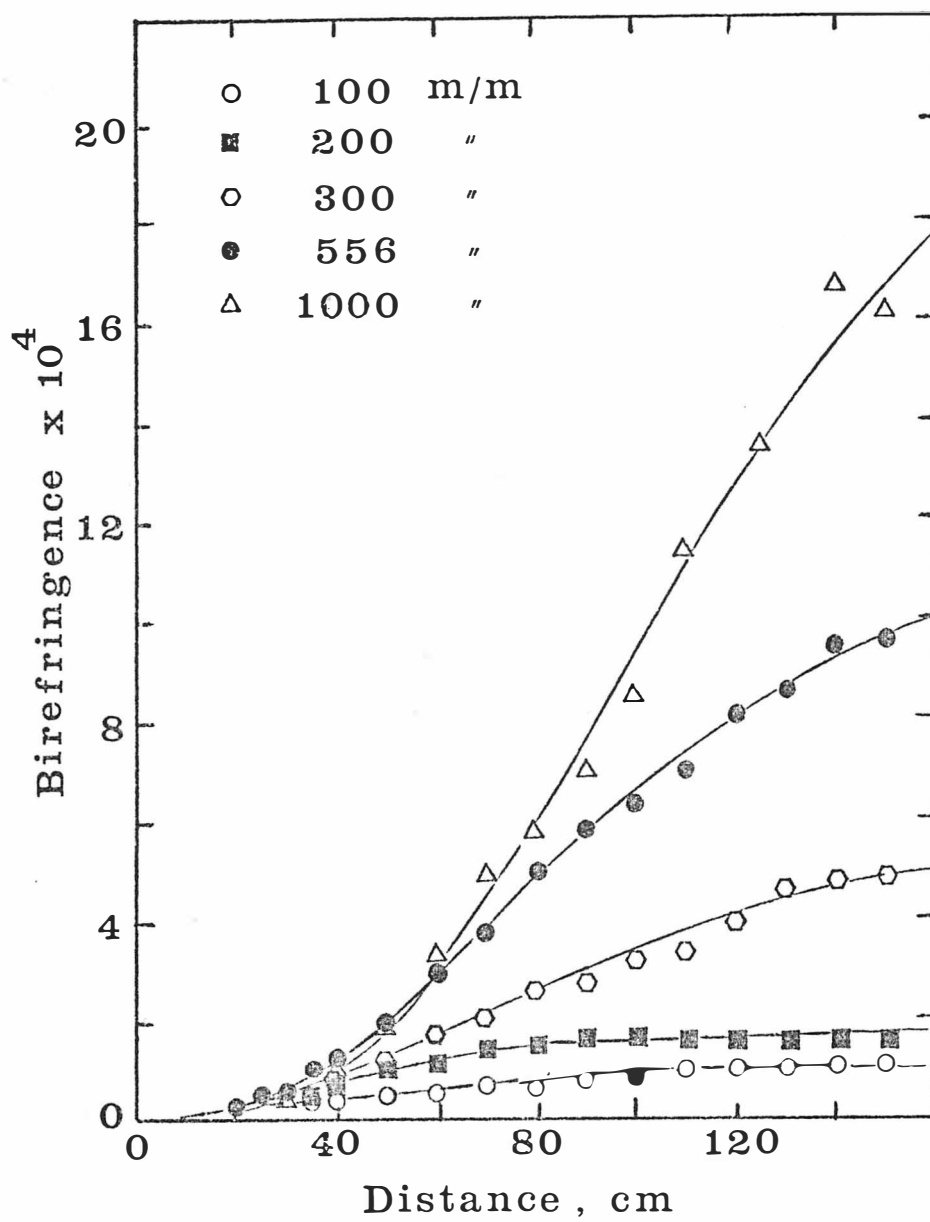


Figure VII-3. Spinline birefringence as a function of distance from the spinneret.

amorphous samples. The results of the present studies thus indicate that the nylon-6 remains amorphous on the spinline even when the take-up velocity was increased to 1000 m/min. This result did not change even after spinning nylon-6 in wet saturated air, as is evident from Figure VII-2. This is surprising because equilibration with moisture is known to increase the crystallinity of nylon-6 (64). However, one must remember that the residence time of nylon-6 molecules in the humid atmosphere is very short, no more than one second. This time does not seem to be enough to produce crystallization in the spinline.

The absence of crystallinity in the spinline of nylon-6 is in complete contrast with the results on high density polyethylene and polypropylene spinline where crystallinity as high as 30-60 percent was observed. This is, of course, due to quite high rates of crystallization of polyolefins compared to nylon-6. For example, the half times of isothermal quiescent crystallization of HDPE (26) and nylon-6 (77) with 10° undercooling are 9.3 minutes and 90 minutes respectively.

The birefringence in the spinline steadily increases from zero in the molten region near the spinneret to a steady value for fibers at low take-up velocities. The birefringence is greater at higher take-up velocities and keeps on increasing even when the fiber velocity gradient becomes zero. The temperature of the fiber in this region is above the glass transition temperature. Therefore, large spinline stresses at higher take-up velocities could continue to cause molecular rearrangement in the fiber and continued alignment of the molecules parallel to the fiber axis and thereby increase the birefringence.

It is also possible that the increase in birefringence is due

to incipient formation of pseudo-hexagonal crystallites. However, the size of such incipient crystallites is too small to obtain any detectable crystalline interference effects on the on-line WAXS patterns.

B. STRUCTURAL CHARACTERISTICS OF SPUN FIBERS

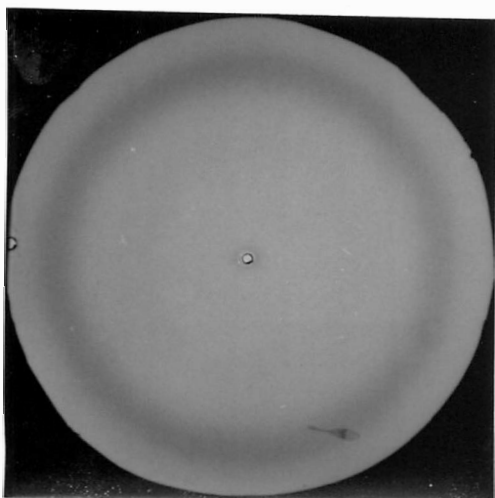
Results

WAXS patterns of spun fibers were taken in a vacuum camera immediately after spinning. The time required to take the sample from the bobbin and put it in a vacuum camera was less than five minutes. These patterns are shown in Figure VII-4.

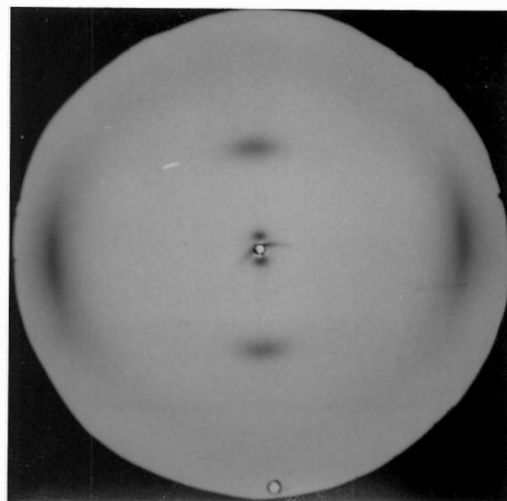
Figure VII-5 shows effects of conditioning the samples at 65 percent relative humidity for 24 hours on WAXS. The effect of conditioning on the birefringence of the sample is seen in Table 8. The birefringence of the conditioned samples is plotted in Figure VII-6 against the spinline stresses.

The crystalline orientation of the spun and conditioned fibers was determined using an x-ray diffractometer. Hexagonal symmetry of the unit cell was assumed in the spun fibers. The a- and b-axes of a hexagonal cell are crystallographically equivalent. Therefore it is not possible to determine separate a- and b-axis orientation functions. We assume that $f_a = f_b$. This value, as well as f_c , are plotted in Figure VII-7 against take-up velocity and in Figure VII-8 against spinline stress. The f_c was obtained using Wilchinsky's analysis for a hexagonal unit cell. This gives

$$f_c = -2f_a \quad (\text{VII-1})$$

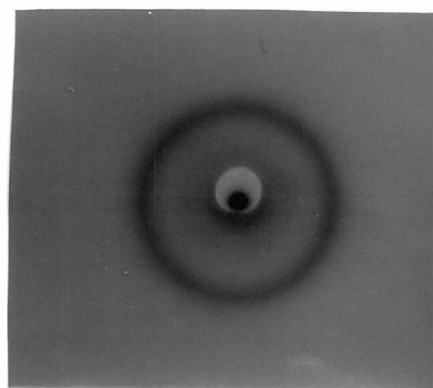


(A) 200 m/min

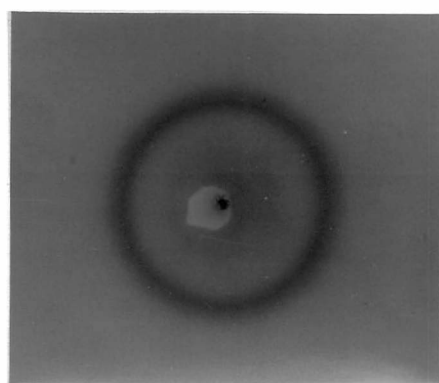


(B) 1000 m/min

Figure VII-4. WAXS patterns of nylon-6 fibers taken immediately after spinning.



(A) 0 Hours



(B) 24 Hours

Figure VII-5. WAXS patterns of nylon-6 fibers spun at 100 meters per minute and conditioned at 65 percent relative humidity for different lengths of time.

TABLE 8

BIREFRINGENCE OF NYLON-6 FIBERS IN THE SPINLINE (MAXIMUM
VALUE) AND AFTER CONDITIONING AT 65 PERCENT RELATIVE
HUMIDITY FOR 24 HOURS

Take-up Velocity Met/min	Maximum Birefringence in the Spinline $\times 10^5$	Birefringence of Conditioned Fibers $\times 10^5$
100	9	110
200	15	450
300	47	700
556	97	1500
1000	172	2280

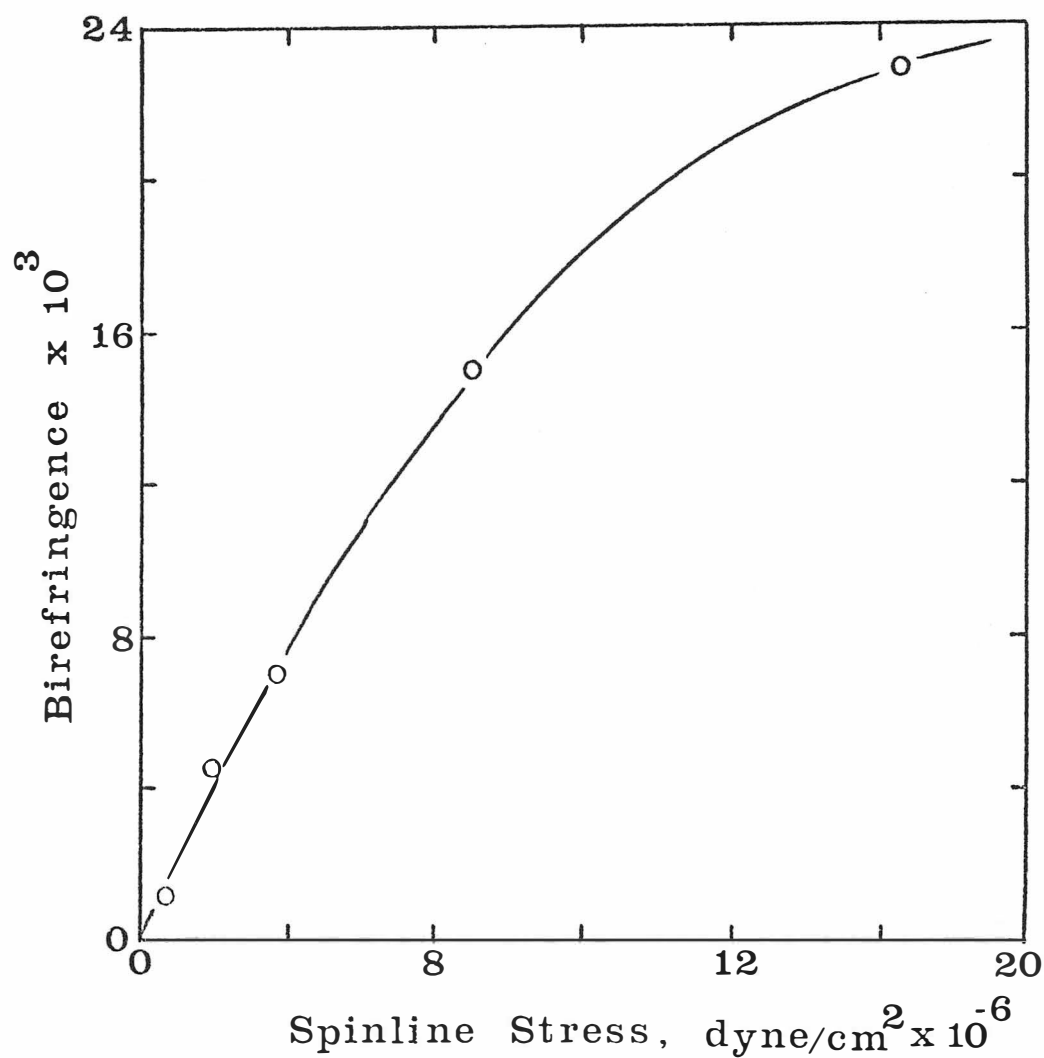


Figure VII-6. Birefringence of nylon-6 fibers conditioned for 24 hours at 65 percent relative humidity plotted as a function of spinline stress.

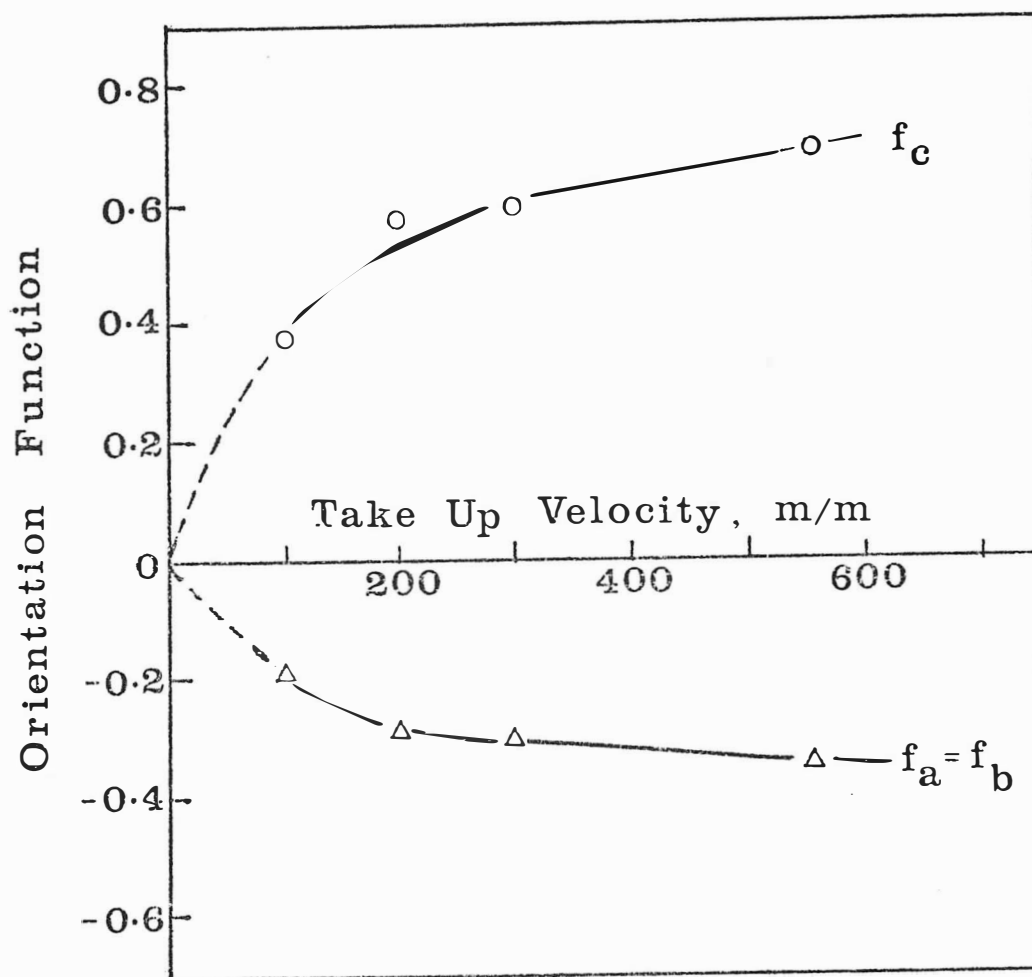


Figure VII-7. Orientation function of spun and conditioned nylon-6 fibers as a function of take-up velocity.

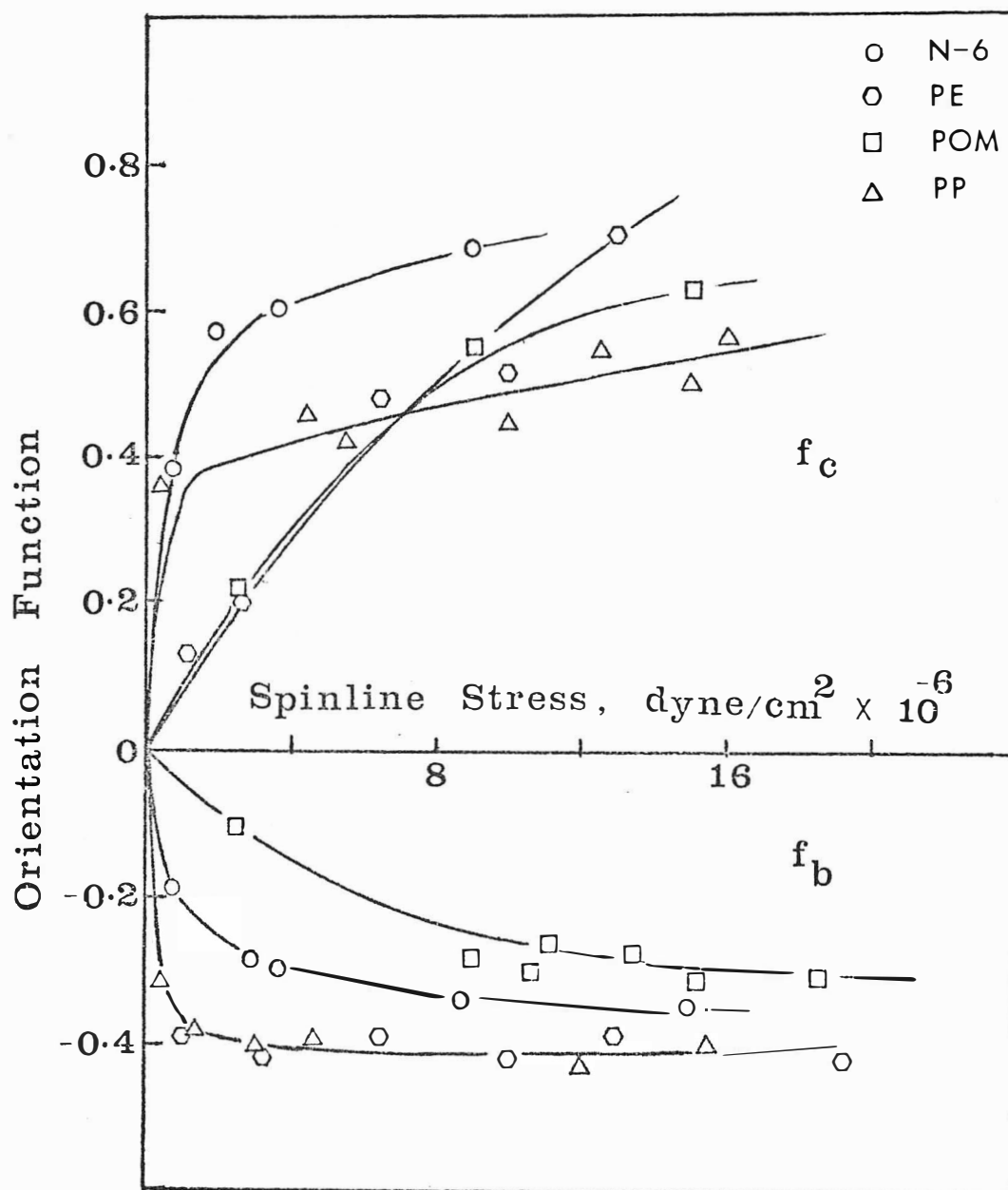


Figure VII-8. Orientation function of spun fibers of nylon-6, polyethylene, polyoxymethylene and polypropylene as a function of spinline stress.

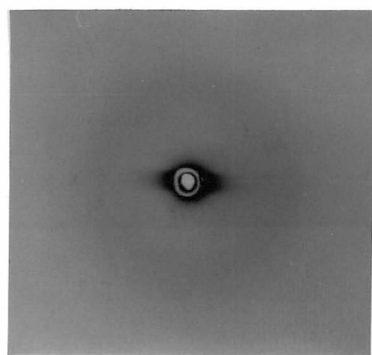
In Figure VII-9, SAXS patterns of the samples spun at different take-up velocities are shown.

Discussion

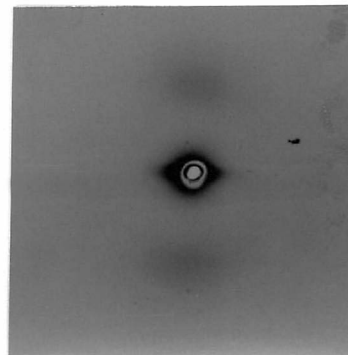
It is seen in Figure VII-4 that the sample spun at 200 meters/minute shows an amorphous halo with $d_{\text{avg}} = 4.23\text{\AA}$, and the samples spun at 1000 meters/minute exhibits a pattern characteristic of a well oriented γ -form with small crystal size. This difference seems to be due to the higher rate of nucleation caused by higher molecular orientation in the latter sample. This higher molecular orientation was generated as a result of the higher spinline stress developed by the high take-up rate. Thus, although nylon-6 does not crystallize on the spinline, it does so on the bobbin, and the rate of this process depends on the molecular orientation developed by the spinning conditions.

If the samples which are initially amorphous are conditioned in a humid atmosphere, for a sufficiently long time, they crystallize into a γ -form. This is seen in Figure VII-5 where the conditioned sample shows a distinct crystalline ring within the amorphous halo. This increase in crystallinity has been observed by other investigators also and is attributed to the plasticizing action of water molecules which increase the chain mobility.

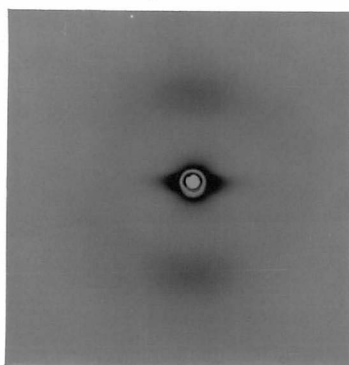
The process of conditioning also causes an increase in the molecular orientation of nylon-6 fibers. This is obvious from Table 8 where the birefringence of the conditioned fibers is seen to be ten to fifteen times higher than the highest birefringence values observed in the spinline.



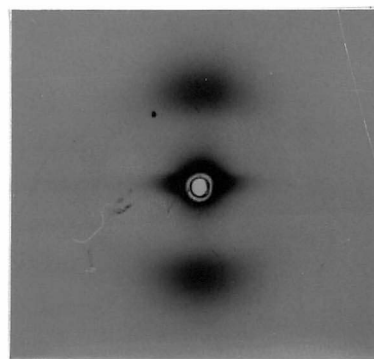
(A) 100 m/min



(B) 200 m/min



(C) 556 m/min



(D) 1000 m/min

Figure VII-9. SAXS patterns of spun and conditioned nylon-6 fibers.

The molecular orientation of the spun and conditioned samples depends on the spinline stress. This is strikingly seen in Figure VII-6. As in the case of other polymers (48, 89), nylon-6 also shows an increase in birefringence with spinline stress.

The crystalline orientation factor f_c , shown in Figures VII-7 and VII-8, increases with take-up velocity and spinline stress, but f_b decreases. Thus as the take-up velocity or the spinline stress increases, the c-axes tend to become more nearly parallel to the fiber axis, while the b-axes (or a-axes) tend to become more nearly perpendicular to the fiber axis.

For comparison, f_b and f_c values for polyethylene (PE) (48), polypropylene (PP) (68), and polyoxymethylene (POM) (89) fibers are also shown in Figure VII-9. In case of PE and PP, f_b drops to about -0.4 and the b-axis becomes nearly perpendicular to the fiber axis even at very low stress level. For nylon-6 and POM (hexagonal unit cell), f_b decreases slowly with spinline stress.

In the case of PE and PP (orthorhombic and monoclinic unit cells, respectively), one can uniquely determine f_a and f_b from separate x-ray data. For nylon-6 and POM, we cannot distinguish between the a- and b-axis. In determining f_a or f_b for the hexagonal unit cell, the intensity distribution for the (100) reflections is in effect averaged with the distribution from the (010) reflections. The net effect is that the measured value of f_a (or f_b) represents the average orientation of both the a- and b-axes in the fiber. Thus, no conclusion can be drawn from the fact that this value decreases more slowly than the value of f_b for PE and PP.

Interestingly enough, the f_c values for PE and POM are nearly equal in the low stress region and increase slowly with spinline stress, but those for PP and nylon-6 increase rather sharply to a value of about 0.4 and then increase slowly.

The SAXS patterns in Figure VII-9 show that for 100 m/min sample, there is a nearly uniform diffuse ring, but at high take-up velocities, typical two point diagrams are obtained. The long period spacings obtained from these patterns are listed in Table 9. They lie in the range of $60-65\text{\AA}$. This can be compared with the value of $60\text{\AA}$ obtained by Geil (60) for single crystals of nylon-6. The long period spacings of nylon-6 are much smaller than those of polyethylene or polypropylene which are about $230\text{\AA}$ and $135\text{\AA}$ respectively.

Possible Morphological Interpretation

The SAXS of nylon-6 spun at low take-up velocity (100 m/m) shows a diffuse ring. This is indicative of an unoriented lamellar structure, probably spherulitic structure. The SAXS of nylon-6 at high take-up velocities shows a two point diagram. This suggests a row nucleated structure with lamellae growing perpendicular to the fiber axis. These lamellae consist of alternate crystalline and amorphous regions. The chains in the lamellae fold. It may be recalled that the lamellar structure has been observed in the solution crystallized single crystals (60, 123). Infrared studies on the bulk crystallized aliphatic polyamides also suggest the existence of chain folded structure (92). Evidence for chain folding in nylon 66 has been discussed by Dismore and Statton (52). A model of chain folded lamellar structure in the

TABLE 9
LONG PERIOD SPACINGS OF NYLON-6 FIBERS SPUN AT DIFFERENT
TAKE-UP VELOCITIES

Take-up Velocity Met/min	Long Period Spacing A°
100	65
200	65
556	65
1000	63
1500	63
2000	60
2400	65

melt spun nylon-6 fibers thus seems reasonable.

The two point SAXS diagrams of nylon-6 are not very sharp. The intensity spreads slightly from the meridian around the incident beam and sideways. This may mean that the lamellae are not growing strictly perpendicular to the fiber axis, but are slightly tilted. On the other hand, it is also possible that the lamellae are growing perpendicular and are twisting slightly as they grow. In the absence of electron microscopy and due to the impossibility of obtaining definitive orientation data due to the hexagonal symmetry of the nylon-6 (γ -form) unit cell, it is not possible to draw detailed conclusions about the nature of the lamellar morphology. One might speculate that if one indeed has lamellar structure with the c-axis perpendicular to the broad face of the lamella and there is regular twisting of the lamellae about some growth direction (perpendicular to c-axis in the unit cell), the values of f_c and f_a (or f_b) should be +0.25 and -0.125 respectively. If there is less twisting f_c should be greater than +0.25 and f_a be less than -0.125. The f_a or f_b values for POM (hexagonal symmetry) in Figure VII-9 at low stress level (about 3×10^6 dynes/cm²) are about -0.1 indicating the possibility that the lamellae may be regularly twisting at this stress level. At higher stress levels, these values become about -0.3 showing less twisting. For POM there is also electron microscopy indicating lamellar twisting (89).

For nylon-6 $f_a = -0.3$ even at very low stress levels of about 3×10^6 dynes/cm². Thus, it seems that nylon-6 lamellae twist to a lesser extent (if indeed they twist) than PE or POM. This is also evident from f_c values in Figure VII-3. They are lower for PE and POM

than for nylon-6 or even PP in the region of low stress levels.

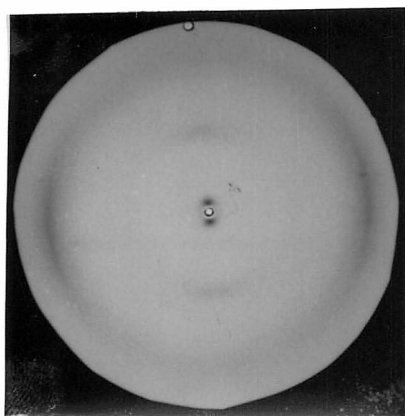
C. POST TREATMENT OF SPUN FIBERS

Results

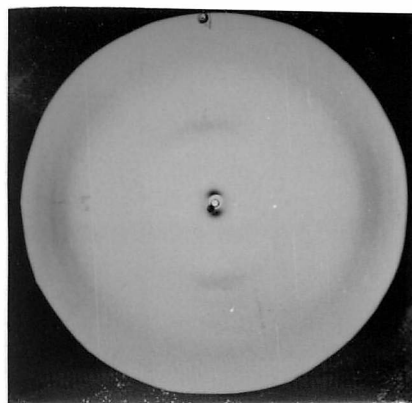
The effects of annealing treatment of spun fibers in water and 20 percent formic acid are shown in WAXS patterns of Figures VII-10 and VII-11. The meridional peak of $8.2\text{\AA}$ slowly disappears and the equatorial peak of $4.13\text{\AA}$ splits into two reflections. The angular difference between these two reflections was studied with the help of an x-ray diffractometer and is shown in Figure VII-12. This transformation becomes more pronounced at higher temperature. At any temperature the formic acid treatment seems to be more effective than annealing either in water or air. Interplanar spacings determined from the angular position of the peak of each observed reflection are given in Table 10. The long period spacings obtained from SAXS are shown in Figure VII-13. It increases at first slowly, but later quite rapidly with temperature.

Discussion

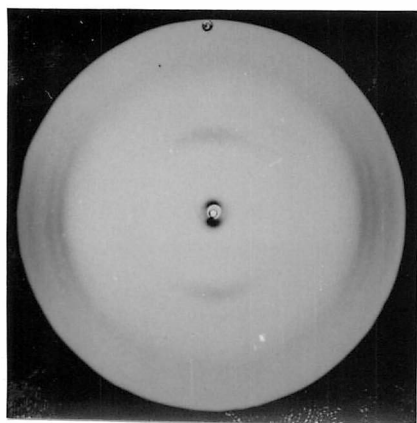
The spun fibers initially showing a pseudo-hexagonal structure changes slowly into a monoclinic structure after annealing. The equatorial peak (100) or (010) of the pseudo-hexagonal structure (γ -form) splits into two peaks, (200) and a doublet (002) (202) of a monoclinic structure (α -form). This α -form is rather imperfect and has been called "paracrystalline α -form" by Roldan and Kaufman (132). The d-spacings of this form are not sharply defined. They vary with



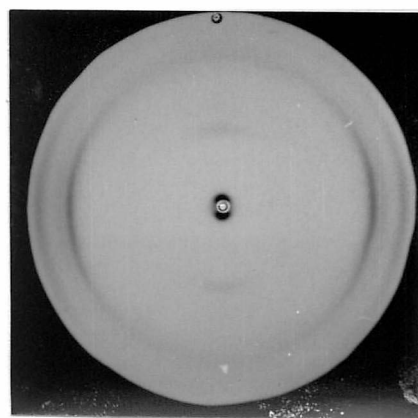
(A) Unannealed



(B) 25°C

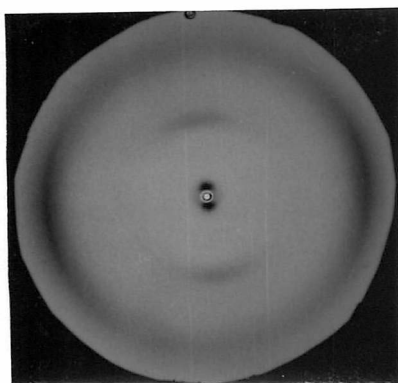


(C) 60°C



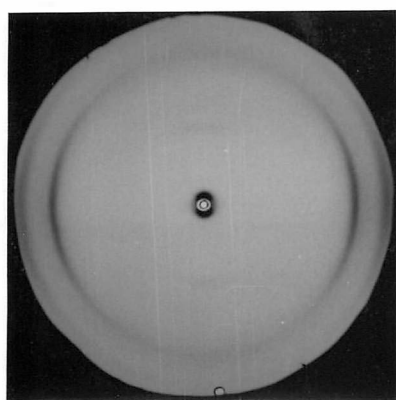
(D) 100°C

Figure VII-10. WAXS patterns of nylon-6 fibers annealed in water at different temperatures for two hours.



(A) Unannealed

(B) 25°C



(C) 75°C

(D) 102°C

Figure VII-11. WAXS patterns of nylon-6 fibers annealed in 20 percent formic acid at different temperatures for two hours.

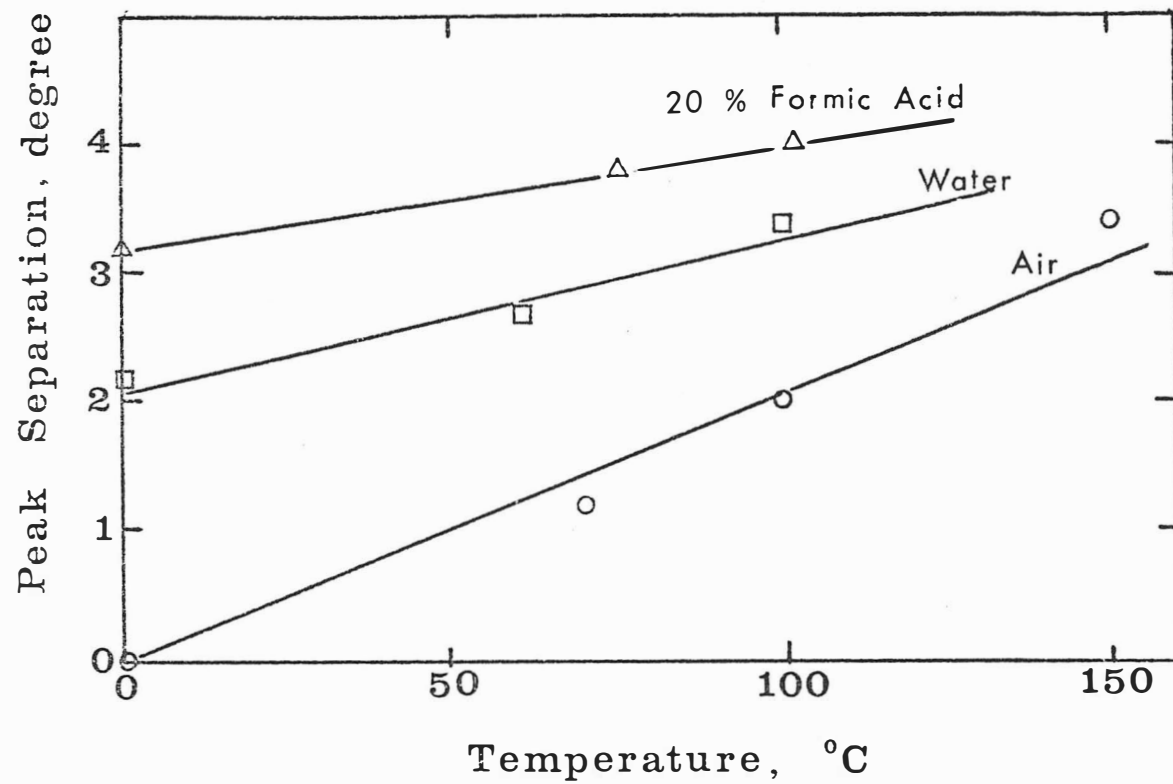


Figure VII-12. Angular separation between (200) and (002) (202) peaks as a function of annealing temperature.

TABLE 10

CHARACTERISTICS OF SPUN AND ANNEALED NYLON-6 FIBERS --
 TAKE-UP SPEED = 556 MET/MIN, ANNEALING TIME = TWO HOURS

Annealed in	Annealing Temperature °C	Difference Δ Between the Peaks (002) (202) and (200) degrees	Long Period Spacing Å°	Birefringence $\times 10^3$
Vacuum Oven	25	0.0	64.6	15.0
	70	1.2	66.2	21.4
	100	2.0	70.1	37.7
	150	3.4	92.3	42.1
Water	25	2.2	70.4	20.8
	60	2.7	73.9	27.3
	100	3.4	87.9	30.6
20%	25	3.2	75.6	30.3
Formic Acid	75	3.8	82.6	49.6
Solution	102	4.0	89.5	66.8

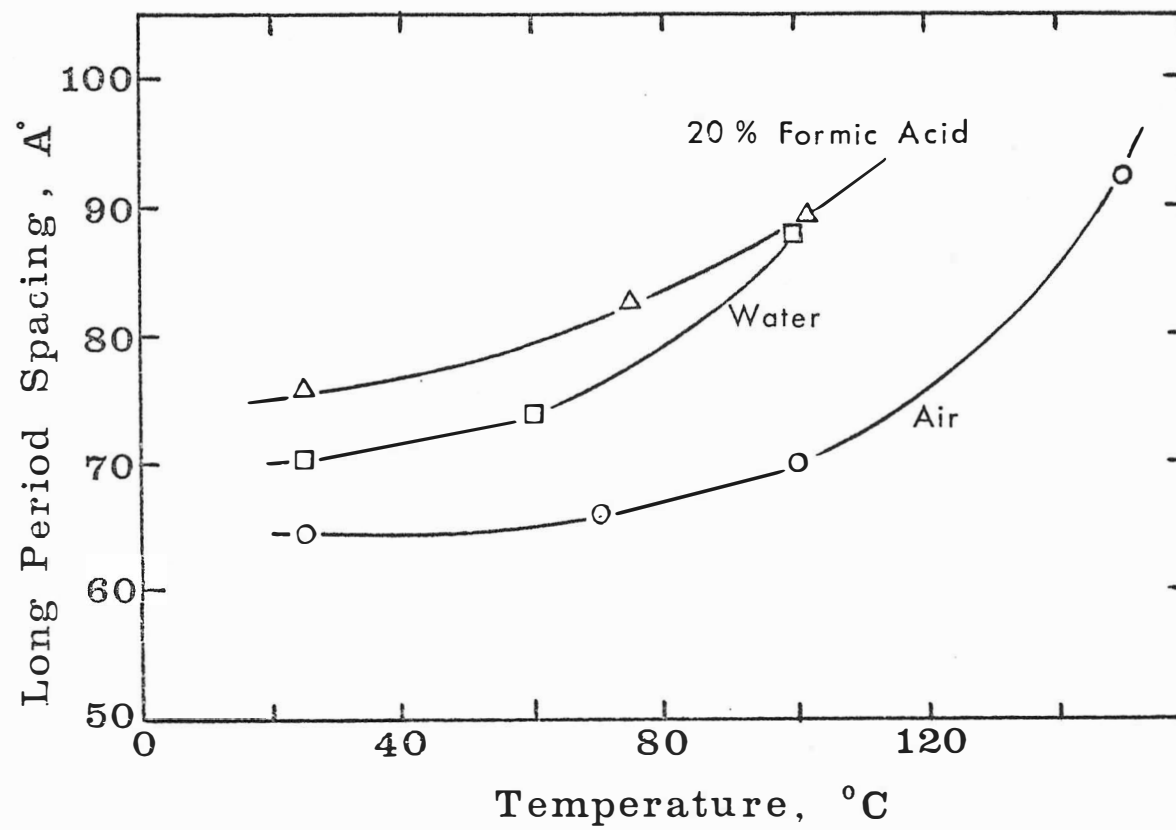


Figure VII-13. Long period spacings as a function of annealing temperature.

the annealing treatment.

The plot of angular difference between the two equatorial peaks of the α -form as a function of annealing temperature in Figure VII-12 again shows that the most rapid transformation into the α -form occurs in 20 percent formic acid. The transformation is much slower when annealing in air. The rate of transformation increases with temperature for all three media. The annealing in formic acid at about 100°C yields an α -form with about 4° angular separation. This corresponds to the value obtained for Bunn- α form.

The reason for higher rate of transformation in formic acid than in water or in air must be due to ease of breaking of hydrogen bonds by the medium. This allows chains in the crystallites to rearrange themselves. Concentrated formic acid dissolves nylon-6. This would seem to substantiate this suggestion.

CHAPTER VIII

MECHANICAL PROPERTIES OF SPUN NYLON-6

A. RESULTS

The tensile properties of spun fibers conditioned in 65 percent relative humidity environment at 20°C for 24 hours were measured on an Instron Tensile Tester. Typical engineering stress-elongation data obtained are shown for different take-up velocities in Figure VIII-1, while Figure VIII-2 shows corresponding data for the natural draw ratio. Various tensile properties such as tensile strength (based on the initial cross-sectional area), tangent modulus (= initial slope of the stress-elongation curve and elongation at break were obtained from these data. These are plotted in Figures VIII-3 through VIII-6 as functions of various parameters such as take-up velocity and spinline stress

B. DISCUSSION

Figure VIII-1 shows that the fibers spun at low take-up velocities show higher elongation to break, but lower stress (based on original cross-sectional area) at break. They also show a distinct yield point. Such a yield point is not observed for fibers spun at very high take-up velocities (such as 2400 meters/minute).

A natural draw ratio (NDR) or yield elongation can be calculated from the stress-elongation curves of Figure VII-1. This was done

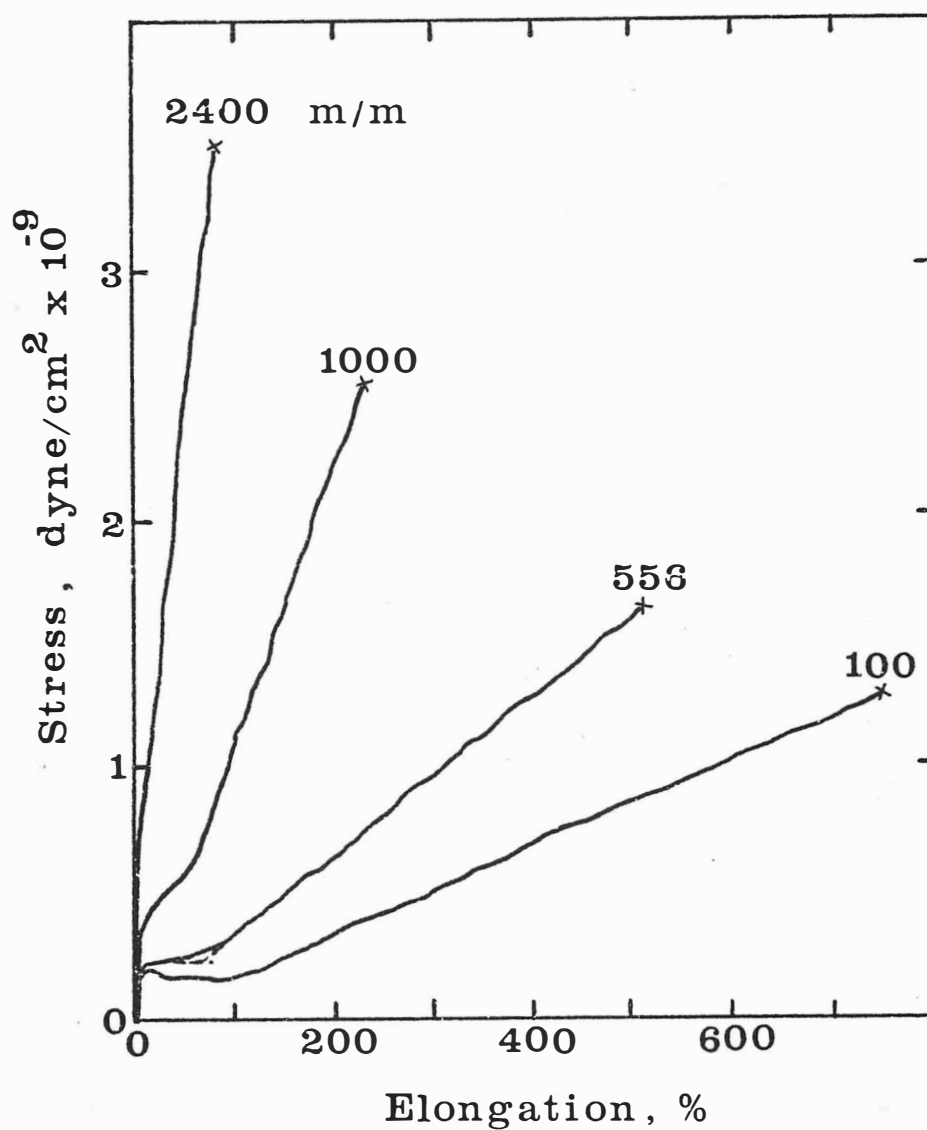


Figure VIII-1. Engineering stress versus elongation of nylon-6 fibers spun at different take-up velocities.

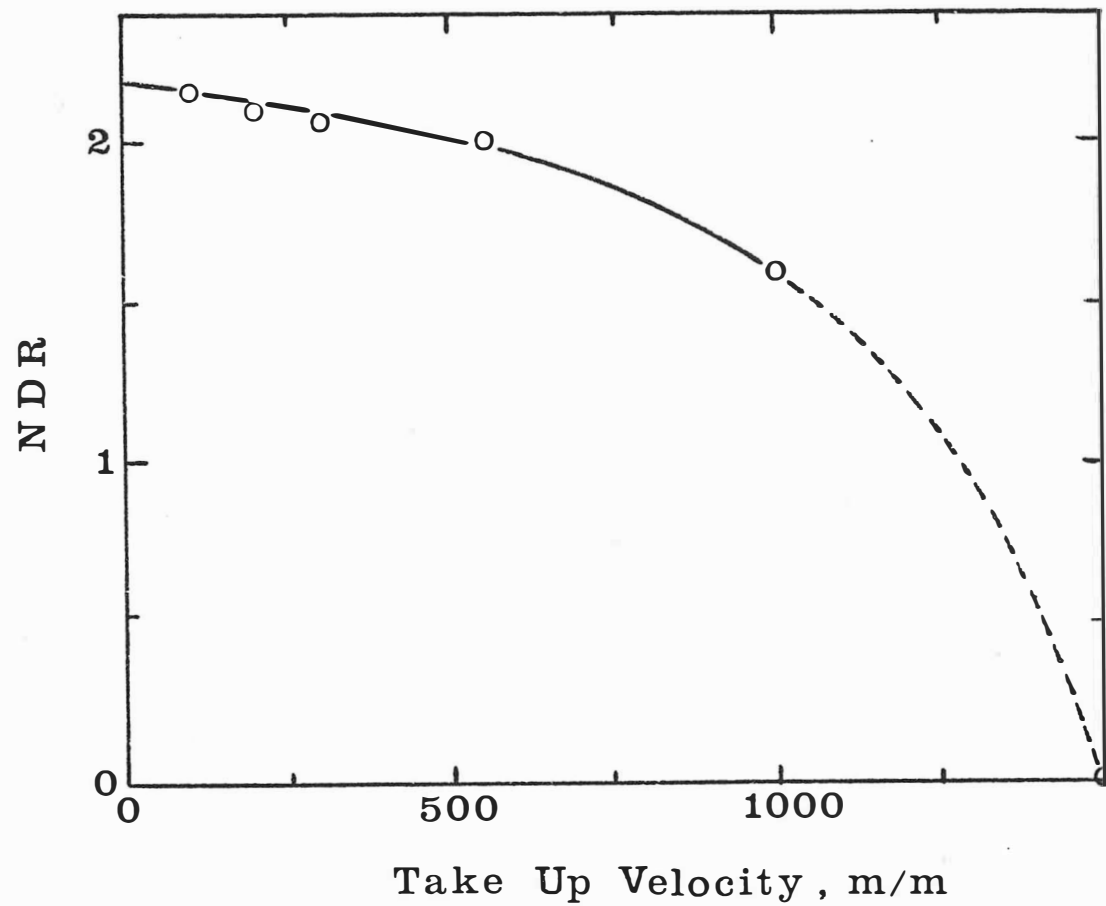


Figure VIII-2. Natural draw ratio (NDR) of spun nylon-6 fibers as a function of take-up velocity.

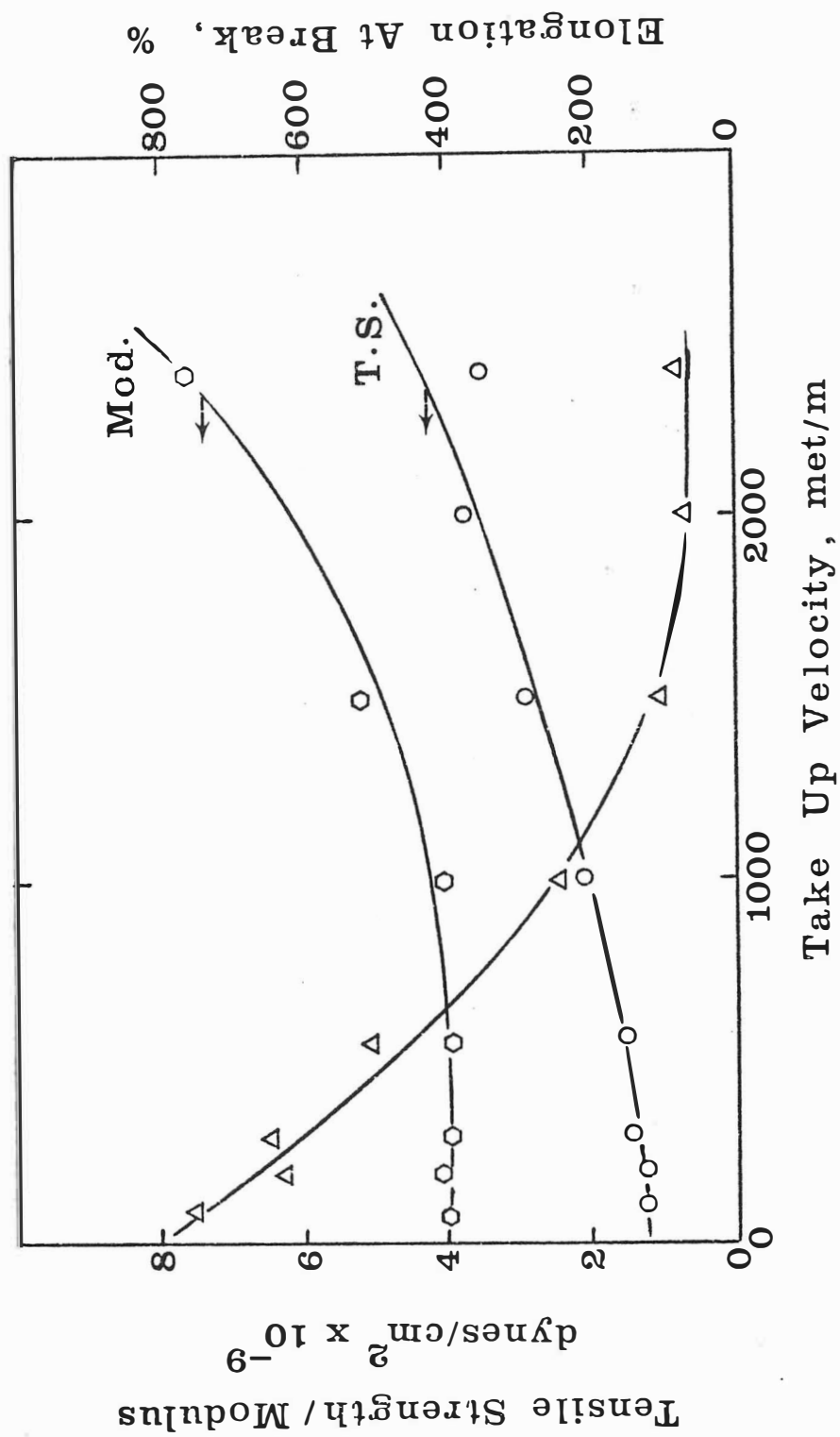


Figure VIII-3. Tensile properties of spun nylon-6 fibers as a function of take-up velocity.

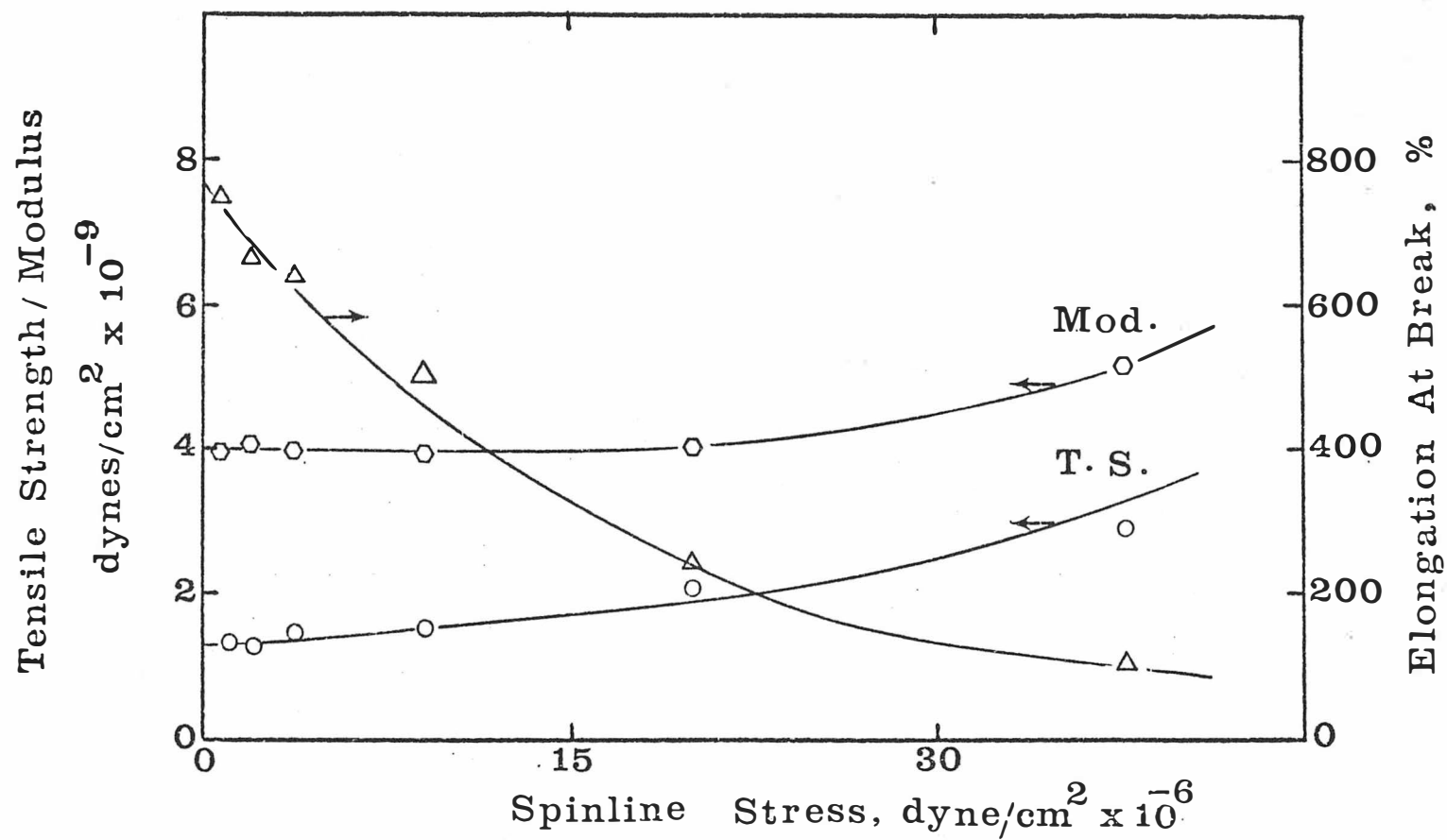


Figure VIII-4. Tensile properties of spun nylon-6 fibers as a function of spinline stress.

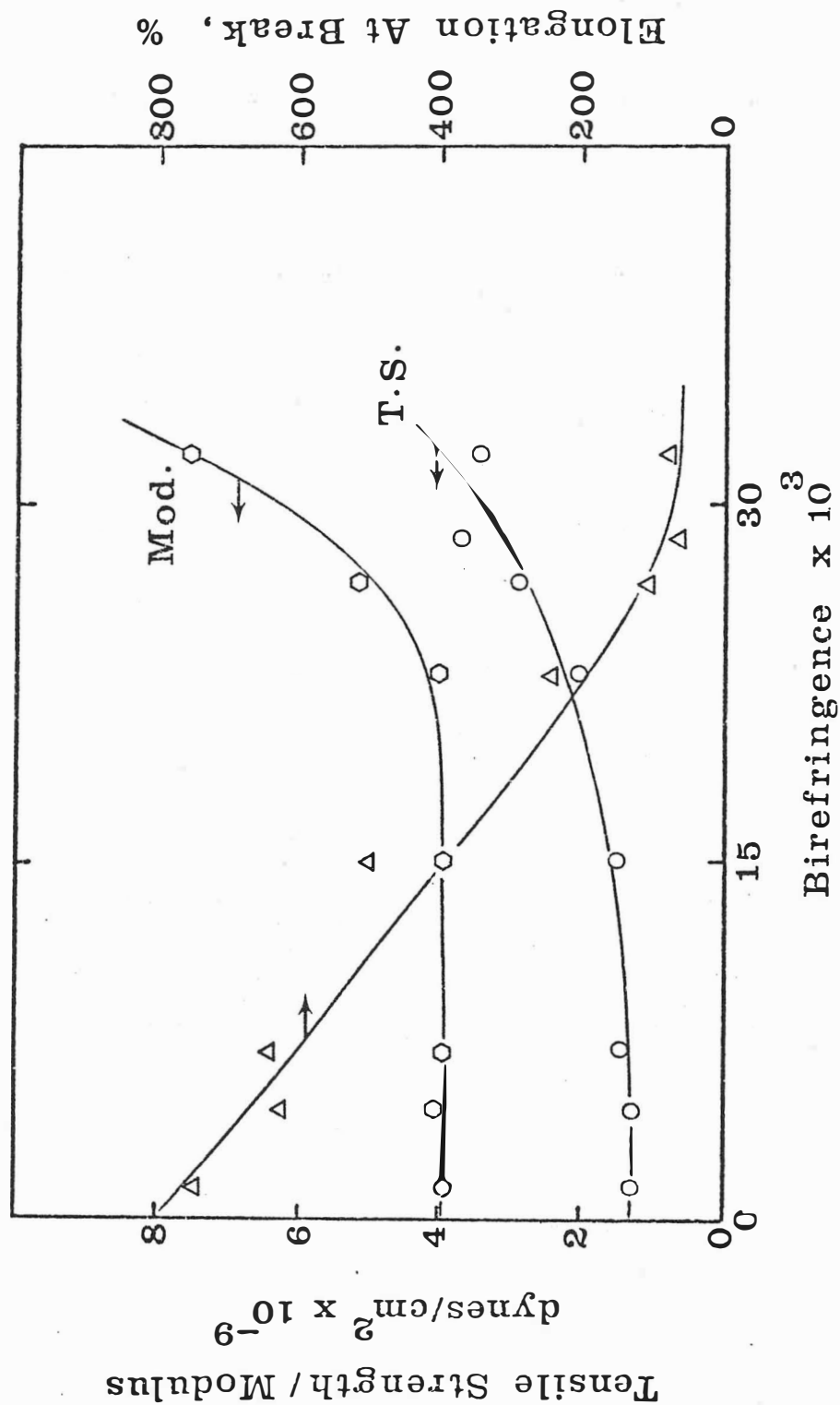


Figure VIII-5. Tensile properties of spun nylon-6 fibers as a function of birefringence.

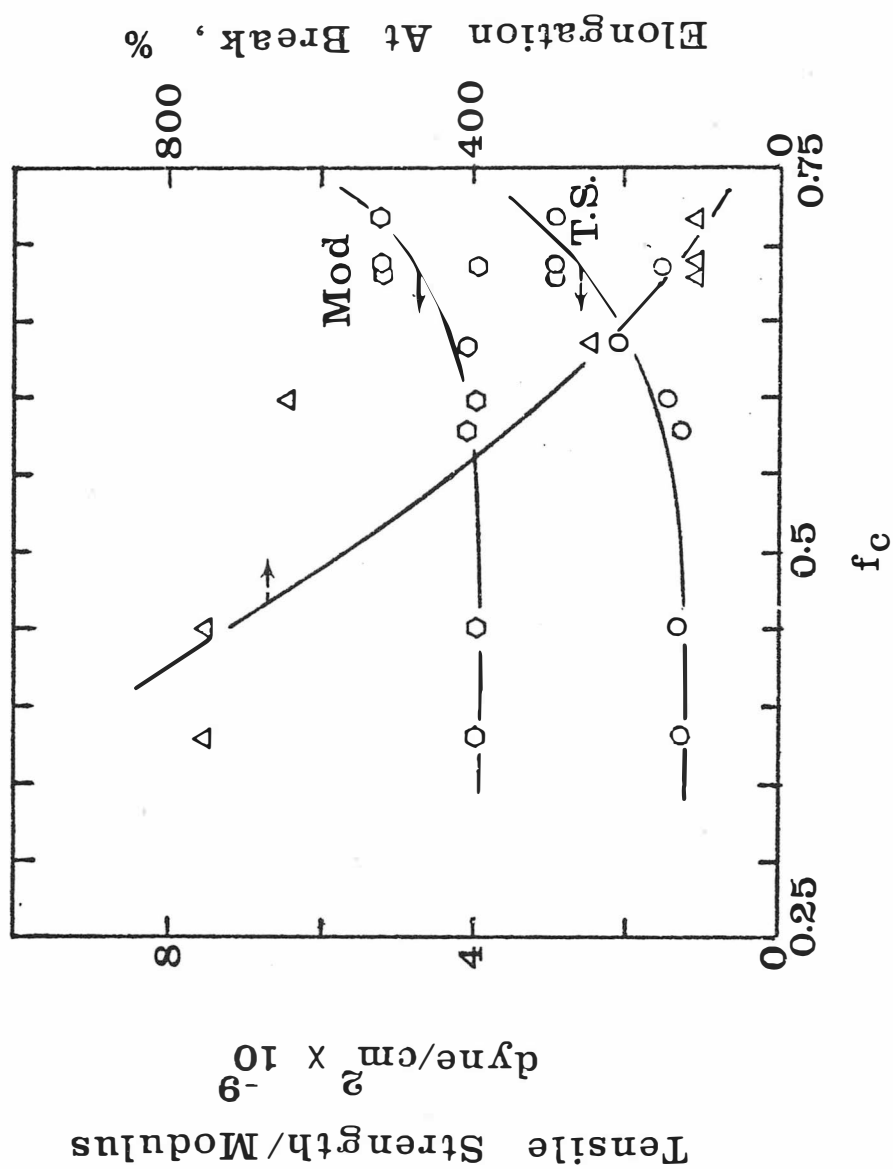


Figure VIII-6. Tensile properties of spun nylon-6 fibers as a function of c-axis orientation factor.

by extrapolating the part of the curve which shows the yield point and allowing it to intersect with the extrapolated part of the straight line portion of the curve beyond the yield point. (This extrapolation is shown in Figure VIII-1 for the curve of 556 meters/minute.) The elongation at the point of intersection gives the NDR. This is plotted in Figure VIII-2 as a function of take-up velocity. It is seen that the NDR decreases with take-up velocity and goes to zero at high take-up velocities.

Figure VIII-3 shows that the tensile strength and the modulus increase with increasing take-up velocity. The modulus increases slowly initially, but much faster when the take-up velocity is increased beyond 1000 meters/minute. The tensile strength increases almost linearly with take-up velocity. The elongation at break decreases with take-up velocity. The decrease is much slower in the high take-up velocity region.

In earlier studies (178, 37, 38), spinline stress was shown to be the primary variable in determining the morphology and the physical properties of spun polyethylene and polypropylene fibers. For this reason the tensile properties of nylon-6 are plotted against spinline stress in Figure VIII-4. The properties vary in the same manner with the spinline stress as with the take-up velocity.

Figure VIII-5 and VIII-6 show that the tensile strength and the modulus initially increase very slowly with structural characteristics of fiber such as birefringence and c-axis orientation factor, f_c , but the increase is much sharper in the region of high values of birefringence and f_c .

In Figures VIII-7 and VIII-8 we have compared the tensile properties of nylon-6 with those of polyethylene (48) and polypropylene (68). The changes in the properties with spinning conditions are similar for all polymers. In general, nylon-6 is found to have a higher tensile strength but lower elongation to break than both polyethylene and polypropylene. However, we must be cautious in making such comparison because the tensile properties of polymers depend heavily on their molecular weights, and there is a very wide difference in the molecular weights of polyamides and polyolefins.

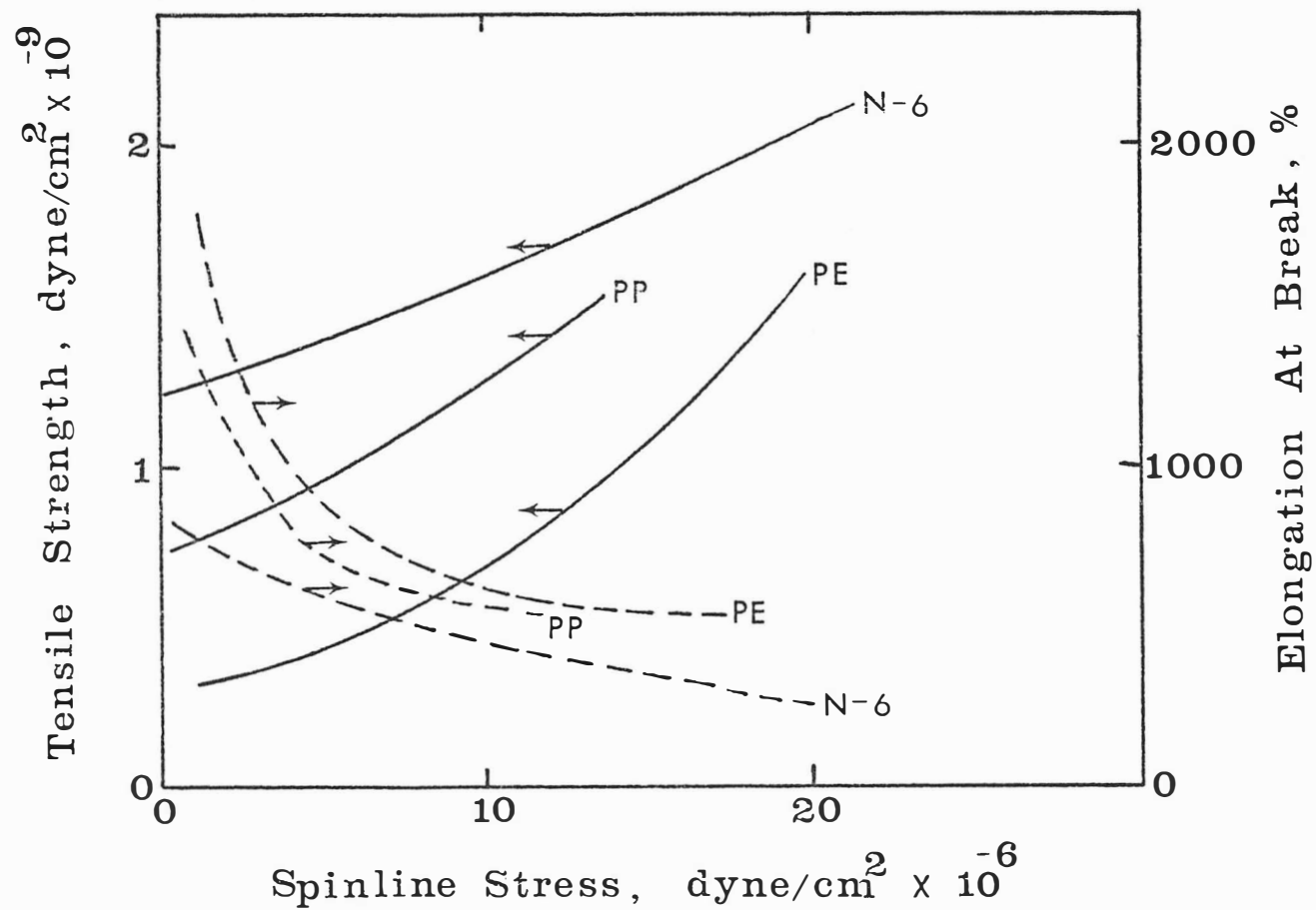


Figure VIII-7. Tensile properties of nylon-6, high density polyethylene and polypropylene fibers as a function of spinline stress.

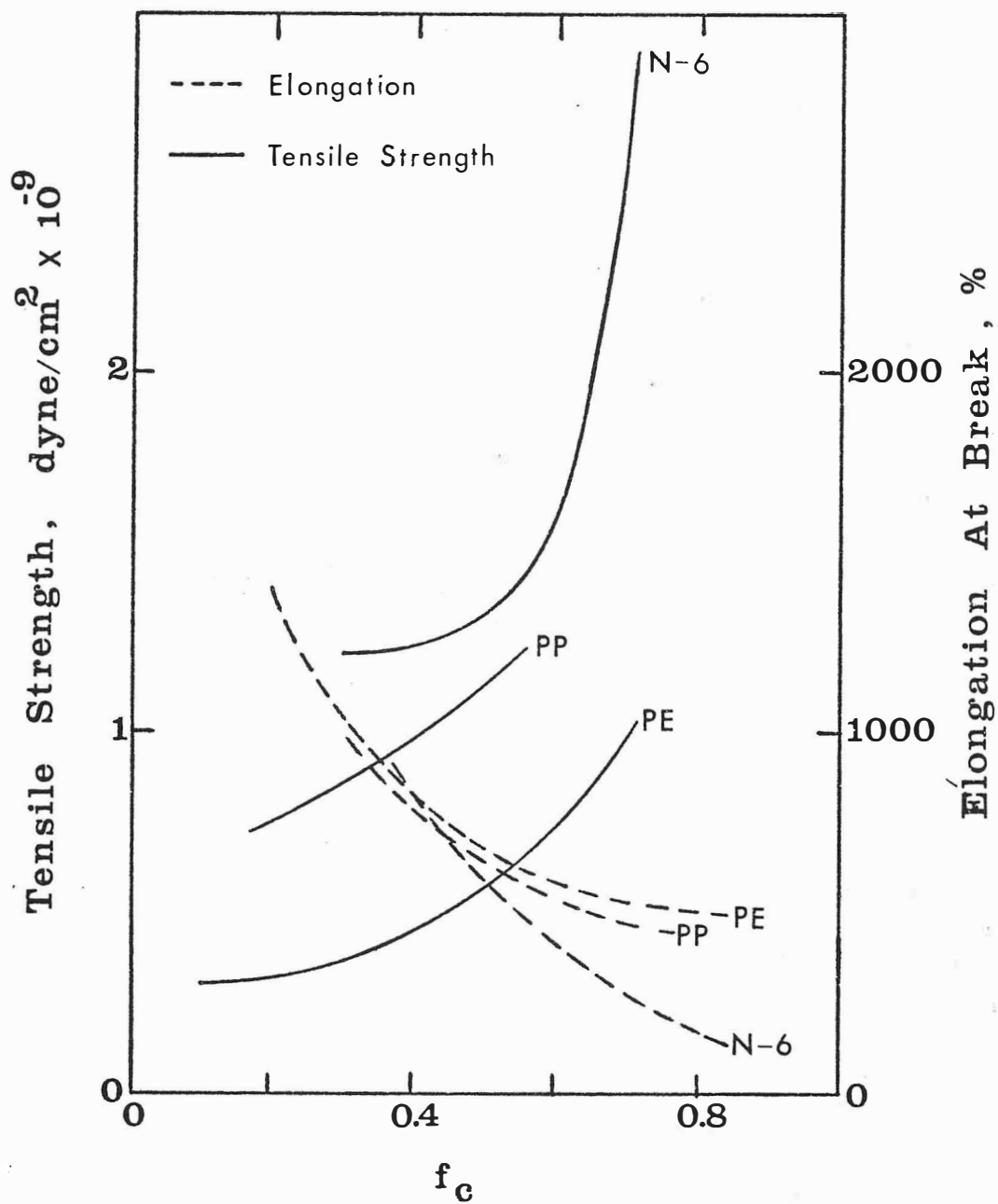


Figure VIII-8. Tensile properties of nylon-6, high density polyethylene and polypropylene as a function of c-axis orientation factor.

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

Various aspects of melt spinning of nylon-6 have been studied in this dissertation. The major conclusions reached from this study, as well as recommendations for further study are presented in this chapter.

A. CONCLUSIONS

Rheological Characterization

Nylon-6 melt shows approximately Newtonian behavior in the laminar shear flow experiments at shear rates of 10 sec^{-1} and lower. The shear viscosity decreases with shear rate in the range of 10 - 1000 sec^{-1} . Very low normal stresses are detected in these experiments. The polymer relaxation time measured in the rheogoniometer is of the order of 0.007 to 0.011 sec at 270°C and 0.025 to 0.04 sec at 230°C . The accuracy of measurement of normal stresses is limited due to thermal degradation and flow instability. The Bogue-White rheological model (with a "box" distribution of relaxation spectrum) describes the shear viscosity behavior in the range of shear rate of 0.1 - 1000 sec^{-1} , if the value of constant "a" in the model is chosen as 0.20 .

Non-Isothermal Melt Spinning

The force distribution in the spinline was obtained for wide range of take-up velocities. At low take-up velocities, the inertia force and the aerodynamic drag are negligible, but the gravity force

is significant. At intermediate velocities, the gravity force balances the combined drag and inertia forces. At high take-up velocities, both the inertia force and the aerodynamic drag are significant but the gravity force is negligible. The rheological force decreases along the spinline at low take-up velocities, remains constant at intermediate velocities and increases at high take-up velocities. The aerodynamic drag obtained by using the boundary layer analysis of Sakiadis (135) is much lower than that obtained by using experimental C_f -Re relationships of several other research groups (5, 64, 138).

The non-isothermal elongational viscosity increases exponentially as the fiber temperature is decreased. The results of the spinline spun at different take-up velocities overlap in the high temperature region but spread apart at lower temperatures. The spread is greater if the experimental C_f -Re relationships of Hamana, et al. (84) are used to calculate the drag and the elongational viscosity.

Isothermal Melt Spinning:

Isothermal melt spinning experiments interpreted in terms of elongational viscosities give a χ function which increases with elongation rate. The χ/η ratio of about 15 obtained in the present studies generally agrees with analysis of previously published data on χ and η for separate polymers.

Predictions of elongational viscosity, using various rheological models and material parameters determined in the shear experiments, lie close to the Newtonian predictions. Interpretation of the data in terms of the theory of Denn, Petrie and Avenas for melt spinning of a

convected Maxwell fluid shows that agreement is only possible if we use a value of relaxation time 30 to 40 times greater than the normal stress based average relaxation time.

Structure Development and Morphology

Nylon-6 filaments remain amorphous in the running spinline even at take-up velocities of up to 1500 meters/minute. A humid saturated atmosphere around the spinline does not produce any crystallinity in the running spinline. Birefringence increases along the spinline. At high take-up velocities, the increase persists even at temperatures as low as 80°C and after the filament has reached its final diameter. This behavior is probably caused by an incipient crystallization ordering phenomenon. However, x-ray diffraction patterns do not show any crystalline reflections in this point of the spinline.

Spun nylon-6 filaments crystallize into pseudohexagonal form upon conditioning them in a humid atmosphere. The birefringence also increases tenfold or more on conditioning. The SAXS patterns of fibers spun at intermediate and high take-up velocities show a meridional two-point diagram. At low velocities the intensity of the SAXS reflection spreads more uniformly around the incident x-ray beam.

The c-axis orientation function of the conditioned filaments increases with take-up velocity and spinline stress.

When the spun conditioned filaments are annealed in air, water or 20 percent formic acid at increasing temperatures, the pseudohexagonal structure changes slowly into a monoclinic structure. The change is more severe with water and formic acid treatment. The long period

of lamellar structure increases with increase in annealing temperature.

Mechanical Properties

Fibers spun at low take-up velocities show yield points in their stress-elongation curves, but those spun at extremely high take-up velocities do not show this behavior. The natural draw ratio decreases with increasing the take-up velocity. The tensile strength and the modulus increase slowly at first, but rapidly later, with increase in such process variables as take-up velocity and spinline stress. The elongation to break decreases rapidly at first, but slowly later, with increase in these variables. Similar behavior is observed when these properties are plotted against such structural characteristics as birefringence and c-axis orientation factors of conditioned fibers.

B. RECOMMENDATIONS

(1) A more thorough study of the viscoelastic properties of nylon-6 melts is required. The spectrum of relaxation times should be measured. In addition, more work is needed on the measurement of normal stresses. The sensitivity of the transducers and the normal stress spring should be increased so that the normal stresses could be measured more accurately in the lower shear rate region.

(2) Die-swell of nylon-6 fibers should be measured at different levels of spinline stresses.

(3) A better theoretical and experimental treatment of spinline rheology is needed. As part of this a longer isothermal chamber should be used in the study of isothermal melt spinning.

(4) Aerodynamic drag coefficient should be determined experimentally. A tensiometer with higher accuracy of measurement should be used.

(5) A constant temperature chamber as well as a steam chamber should be used around the spinline to see if nylon-6 would crystallize in the spinline.

(6) Spinneret dimensions, extrusion temperature and extrusion rate should be varied and their effects on the spinline stress, structural characteristics and properties should be studied.

(7) Studies of drawing of nylon-6 fibers and of spin-draw interaction are needed.

(8) Finally, one should study other nylon fibers to see if the conclusions of present studies are true for all polyamides in general.

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APPENDICES

APPENDIX A

APPENDIX A

Calculations of various force components in the force balance equation are as follows.

Gravity Force

The gravity force is written as

$$F_{gr} = \int_x^L \rho g A dx \quad (A-1)$$

The fiber diameter does not change from $x = 160$ cm to the take-up bobbin ($x = L$). Therefore, F_{gr} at $x = 160$ is

$$F_{gr, 160} = \frac{\rho_{160} + \rho_L}{2} \cdot g \cdot A_{160} (L - 160) \quad (A-2)$$

The total length of the spinline, L , in this experiment is 373 cm. The gravity force at successive points above $x = 160$ cm was calculated by trapezoidal rule of integration; thus, e.g.

$$F_{gr, 155} = F_{gr, 160} + \left(\frac{\rho_{155} + \rho_{160}}{2} \right) \cdot \left(\frac{A_{155} + A_{160}}{2} \right) \cdot g \cdot 5 \quad (A-3)$$

The calculations were carried out in this fashion from $x = 160$ cm to $x = 5$ cm. The experimentally obtained profile of diameter was used to calculate the area A , and the temperature profile and the density-temperature relationship were used to obtain the density.

Inertia Force

The inertia force at each point was calculated as

$$F_{\text{inertia}, x} = W(v_L - v_x) \quad (\text{A-4})$$

where W is the mass flow rate.

Aerodynamic Drag

The aerodynamic drag per unit length of a fiber diameter d running at a velocity V can be given by Equation V-2. This can be obtained with Equation V-3 and integrated to yield

$$F_{\text{aero}} = \frac{m\pi}{2} \rho_a^{1-n} \cdot \mu_a^n \int_0^L v^{2-n} d^{1-n} dx \quad (\text{A-5})$$

Procedure exactly the same as that used in the calculations of the gravity force was used to calculate the drag force. Values of m and n required for these calculations are listed in Table 4, page 79.

The drag force was also calculated by using the Sakiadis analysis. This analysis is carried out for a cylinder of constant diameter running at a constant velocity. In fiber spinning, both of them vary. For this reason, average values of diameter and velocity are used. The average was calculated as

$$v_{\text{avg}} = \frac{1}{n} \sum_{i=1}^n v_i \quad d_{\text{avg}} = \left(\frac{4Q}{\pi v_{\text{avg}}} \right)^{1/2} \quad (\text{A-6})$$

The dimensionless parameter ξ given by Equation II-45b, was calculated

and the numerical solution of Sakiadis was used to obtain the momentum area Θ from ξ . The total drag on the filament between $x = 0$ and $x = x$ is given by Equation II-45a.

The force balance (Equation II-44) on the spinline is made between $x = x$ and $x = L$ (see Chapter II). Therefore the drag must be obtained on this length of the fiber. This is done as

$$F_{x, L} = F_{0, L} - F_{0, x} \quad (A-7)$$

where $F_{x, L}$ denotes drag on the filament between $x = x$ and $x = L$.
 $F_{0, L}$ and $F_{0, x}$.

APPENDIX B

TABLE 11

EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6 NON-ISOTHERMAL SPINNING--
TAKE-UP VELOCITY = 100 MET/MIN, TAKE-UP TENSION = 147 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Temper- ature °C	Fiber Density gm/cc	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	Force Distribution within the Spinline, Dynes						Elongational Viscosity Poise x 10 ⁻⁵		Bire- fringe- nce		
						F _{grav}	F _{iner}	F _{drag}		F _{rheo}		HMK	Sakiadis		HMK	Sakiadis
								HMK*	Sakiadis**	HMK	Sakiadis					
10	4.15	271	0.977	31.5	3.47	100.1	5.7	20.6	12.5	221.8	228.9	0.47	0.49	--		
20	2.75	251	0.987	71.1	4.39	90.7	4.0	20.5	12.4	214.2	221.3	0.82	0.85	--		
30	2.20	231	0.998	109.8	3.79	85.9	2.4	20.2	12.1	211.0	218.4	1.46	1.52	--		
40	1.93	210	1.008	141.3	3.27	82.6	1.1	19.8	11.7	209.7	216.8	2.18	2.25	2.8		
50	1.79	197	1.015	163.1	1.19	79.9	0.0	19.3	11.3	208.6	215.6	6.92	7.19	3.8		
60	1.73	177	1.025	167.0	0.47	77.5	0.0	18.7	10.9	206.8	213.6	18.63	19.34	4.7		
70	1.73	167	1.030	167.0	0.00	75.1	0.0	18.2	10.5	204.9	211.6	∞	∞	5.9		
80	1.73	153	1.037	167.0	0.00	72.7	0.0	17.6	10.1	203.1	209.6	∞	∞	5.7		
90	1.73	144	1.041	167.0	0.00	70.3	0.0	16.0	9.7	201.3	207.6	∞	∞	7.2		
100	1.73	139	1.044	167.0	0.00	67.9	0.0	15.5	9.3	199.5	205.6	∞	∞	7.9		
110	1.73	130	1.049	167.0	0.00	65.5	0.0	14.9	8.9	197.6	203.6	∞	∞	9.3		
120	1.73	118	1.054	167.0	0.00	63.0	0.0	14.3	8.5	195.7	201.5	∞	∞	8.9		
130	1.73	111	1.058	167.0	0.00	60.6	0.0	13.8	8.1	193.8	199.4	∞	∞	8.9		
140	1.73	106	1.061	167.0	0.00	58.1	0.0	13.2	7.8	191.9	197.4	∞	∞	9.6		
150	1.73	101	1.063	167.0	0.00	55.7	0.0	12.6	7.4	190.0	195.3	∞	∞	9.3		
160	1.73	97	1.065	167.0	0.00	53.2	0.0	12.1	7.0	188.2	193.2	∞	∞	8.6		

*HMK: Calculations based on the C_F-Re relationship of Hamana, Matsui and Kato.

**Sakiadis: Calculations based on the Sakiadis analysis of aerodynamic drag.

TABLE 12
EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6 NON-ISOTHERMAL SPINNING--
TAKE-UP VELOCITY = 200 MET/MIN, TAKE-UP TENSION = 215.6 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Temper- ature °C	Fiber Density gm/cc	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	Force Distribution within the Spinline, Dynes						Elongational Viscosity Poise x 10 ⁻⁵		Bire- frin- gence		
						F _{grav}	F _{iner}	F _{drag}		F _{rheo}		HMK	Sakiadis		HMK	Sakiadis
								HMK*	Sakiadis**	HMK	Sakiadis					
10	3.80	270	0.978	37.6	4.07	55.4	12.3	44.0	23.8	214.7	234.9	0.47	0.51	--		
20	2.48	248	0.989	85.2	5.49	47.6	10.3	43.6	23.6	209.1	229.2	0.79	0.86	--		
30	1.90	228	0.999	147.1	5.95	43.9	7.8	43.4	23.3	208.2	228.4	1.23	1.35	--		
40	1.58	206	1.010	210.4	5.12	41.5	5.1	42.5	22.7	209.5	229.3	2.09	2.28	1.8		
50	1.45	188	1.019	247.6	4.01	39.9	3.6	41.4	22.1	210.5	229.8	3.18	3.47	2.1		
60	1.37	171	1.028	275.0	3.64	38.3	2.4	40.3	21.4	211.2	230.1	3.94	4.29	2.4		
70	1.28	155	1.036	312.5	2.88	36.9	0.9	39.2	20.7	212.4	231.0	5.73	6.23	2.7		
80	1.22	146	1.040	333.4	0.93	35.7	0.0	37.9	19.9	213.4	231.4	19.60	21.28	3.0		
90	1.22	137	1.045	333.4	0.00	35.0	0.0	36.7	19.1	213.9	231.5	∞	∞	3.1		
100	1.22	129	1.049	333.4	0.00	33.8	0.0	35.4	18.2	214.0	231.1	∞	∞	3.2		
110	1.22	120	1.053	333.4	0.00	32.6	0.0	34.1	17.5	214.1	230.7	∞	∞	3.2		
120	1.22	111	1.058	333.4	0.00	31.4	0.0	32.7	16.8	214.3	230.2	∞	∞	3.2		
130	1.22	103	1.062	333.4	0.00	30.1	0.0	31.4	15.9	214.3	229.8	∞	∞	3.1		
140	1.22	98	1.065	333.4	0.00	28.9	0.0	30.1	15.2	214.4	229.4	∞	∞	3.1		
150	1.22	93	1.067	333.4	0.00	27.7	0.0	28.8	14.4	214.5	228.9	∞	∞	3.1		
160	1.22	88	1.069	333.4	0.00	26.5	0.0	27.5	13.6	214.6	228.5	∞	∞	3.1		

*HMK: Calculations based on the C_F-Re relationship of Hamana, Matsui and Kato.

**Sakiadis: Calculations based on the Sakiadis analysis of aerodynamic drag.

TABLE 13
EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6, NON-ISOTHERMAL SPINNING--
TAKE-UP SPEED = 300 MET/MIN, TAKE-UP TENSION = 284.2 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Temper- ature °C	Fiber Density gm/cc	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	Force Distribution within the Spinline, Dynes						Elongational Viscosity Poise x 10 ⁻⁵		Bire- frin- gence
						F _{grav}	F _{iner}	F _{drag}		F _{rheo}		HMK	Sakiadis	
								HMK*	Sakiadis**	HMK	Sakiadis			
10	3.75	258	0.984	38.3	4.30	41.2	19.2	68.9	35.3	242.3	270.8	0.51	0.57	--
20	2.20	235	0.996	110.0	6.59	34.0	16.3	68.7	35.1	233.3	266.9	0.93	1.07	--
30	1.75	220	1.003	172.7	6.60	31.0	13.6	68.2	35.7	233.4	265.9	1.47	1.68	--
40	1.48	206	1.010	239.8	7.12	29.0	10.8	67.4	34.1	234.9	268.3	1.92	2.19	2.8
50	1.30	184	1.021	307.5	7.12	27.4	8.0	66.4	33.3	237.2	270.3	2.51	2.86	3.6
60	1.17	166	1.030	376.3	6.80	26.2	5.2	65.1	32.3	240.2	272.9	3.29	3.73	4.5
70	1.08	150	1.038	438.2	6.01	25.2	2.6	63.4	31.3	243.4	275.5	4.42	5.01	5.2
80	1.02	135	1.046	487.5	2.07	24.3	0.5	61.5	30.1	246.5	277.9	14.58	16.43	5.9
90	1.00	126	1.050	500.0	0.00	23.5	0.0	59.4	29.0	248.3	278.7	∞	∞	6.1
100	1.00	119	1.054	500.0	0.00	22.7	0.0	57.3	27.8	249.6	279.1	∞	∞	6.2
110	1.00	110	1.058	500.0	0.00	21.9	0.0	55.2	26.5	250.9	279.5	∞	∞	6.9
120	1.00	104	1.061	500.0	0.00	21.1	0.0	53.1	25.3	252.2	279.9	∞	∞	6.9
130	1.00	100	1.064	500.0	0.00	20.2	0.0	51.0	24.3	253.4	280.2	∞	∞	6.8
140	1.00	95	1.066	500.0	0.00	19.4	0.0	48.9	23.1	254.7	280.6	∞	∞	6.8
150	1.00	90	1.068	500.0	0.00	18.6	0.0	46.8	22.0	256.0	280.8	∞	∞	6.8
160	1.00	86	1.070	500.0	0.00	17.8	0.0	44.7	20.7	257.3	281.2	∞	∞	6.8

*HMK: Calculations based on the C_F -Re relationship of Hamana, Matsui and Kato.

**Sakiadis: Calculations based on the Sakiadis analysis or aerodynamic drag.

TABLE 14
EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6, NON-ISOTHERMAL SPINNING --
TAKE-UP VELOCITY = 556 MET/MIN, TAKE-UP TENSION = 372.4 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Temper- ature °C	Fiber Density gm/cc	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	Force Distribution within the Spinline, Dynes						Elongational Viscosity Poise x 10 ⁻⁵		Bire- frin- gence
						F _{grav}	F _{iner}	F _{drag}		F _{rheo}		HMK	Sakiadis	
								HMK*	Sakiadis**	HMK	Sakiadis			
10	3.70	259	0.983	39	5.42	27.2	36.9	142.7	55.4	219.9	307.2	0.38	0.53	--
20	2.20	236	0.995	110	9.57	20.1	34.0	142.5	55.2	216.0	303.3	0.55	0.77	1.2
30	1.50	219	1.003	235	11.46	17.4	28.8	141.9	54.6	219.1	306.4	1.08	1.51	5.7
40	1.20	196	1.015	363	12.33	16.0	23.5	140.7	53.7	224.2	311.3	1.60	2.23	11.4
50	1.05	175	1.026	469	12.65	15.0	19.0	139.0	52.5	229.3	315.8	2.07	2.86	19.7
60	0.92	154	1.036	605	12.45	14.2	13.4	136.7	51.1	236.5	322.1	2.87	3.91	29.0
70	0.84	139	1.044	720	12.73	13.5	8.6	133.7	49.4	243.6	328.0	3.47	4.67	37.6
80	0.76	130	1.048	876	11.57	13.0	2.1	130.1	47.3	253.3	336.1	4.85	6.44	48.8
90	0.73	122	1.052	926	2.80	12.6	0.0	125.8	44.9	259.2	340.1	21.96	28.83	57.6
100	0.73	114	1.056	926	0.00	12.2	0.0	121.4	42.9	263.1	341.7	∞	∞	62.0
110	0.73	104	1.061	926	0.00	11.7	0.0	117.1	40.7	267.1	343.4	∞	∞	68.0
120	0.73	96	1.065	926	0.00	11.3	0.0	112.7	38.6	271.0	345.1	∞	∞	80.2
130	0.73	91	1.068	926	0.00	10.8	0.0	108.3	36.3	274.9	347.0	∞	∞	85.7
140	0.73	85	1.071	926	0.00	10.4	0.0	103.9	34.2	278.9	348.6	∞	∞	94.3
150	0.73	82	1.073	926	0.00	10.0	0.0	97.6	32.2	284.8	350.1	∞	∞	96.0
160	0.73	78	1.075	926	0.00	9.5	0.0	93.2	30.0	288.7	351.9	∞	∞	97.9

*HMK: Calculations based on the C_f -Re relationship of Hamana, Matsui and Kato.

**Sakiadis: Calculations based on the Sakiadis analysis of aerodynamic drag.

TABLE 15

EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6, NON-ISOTHERMAL SPINNING--
TAKE-UP SPEED = 1000 MET/MIN., TAKE-UP TENSION = 470.4 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Temper- ature °C	Fiber Density gm/cc	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	Force Distribution within the Spinline, Dynes						Elongational Viscosity Poise x 10 ⁻⁵		Bire- frin- gence
						F _{grav}	F _{iner}	F _{drag}		F _{rheo}				
								HMK*	Sakiadis**	HMK	Sakiadis	HMK	Sakiadis	
10	3.40	270	0.970	47	6.10	20.3	67.5	267.4	109.3	155.8	313.9	0.28	0.57	--
20	2.18	242	0.992	113	9.00	14.2	64.8	267.2	109.0	149.9	310.8	0.45	0.93	--
30	1.57	213	1.007	214	10.75	11.4	60.6	266.6	108.5	154.7	312.7	0.74	1.50	3.4
40	1.24	191	1.018	339	13.68	9.8	55.3	265.6	107.7	159.3	317.2	0.96	1.92	9.3
50	1.00	175	1.026	517	18.10	8.8	47.9	263.8	106.4	167.5	324.9	1.18	2.29	17.3
60	0.79	160	1.033	823	19.70	8.2	35.2	260.8	104.4	182.7	339.0	1.89	3.51	32.8
70	0.71	144	1.041	1011	20.56	7.7	27.3	256.4	102.0	194.4	348.8	2.39	4.28	49.6
80	0.69	129	1.049	1062	20.32	7.3	25.2	251.4	99.4	201.2	353.1	2.65	4.65	57.8
90	0.65	115	1.056	1189	18.94	7.0	19.9	245.8	96.6	211.6	360.9	3.37	5.74	69.5
100	0.60	103	1.062	1333	16.26	6.7	11.6	239.5	93.5	226.0	372.0	4.91	8.08	85.7
110	0.54	94	1.066	1667	10.87	6.4	0.0	231.7	89.6	245.1	387.2	9.85	15.56	114.0
120	0.54	87	1.070	1667	0.00	6.2	0.0	222.9	85.5	253.7	391.1	∞	∞	129.0
130	0.54	86	1.073	1667	0.00	5.9	0.0	214.1	81.5	262.3	394.8	∞	∞	167.0
140	0.54	76	1.076	1667	0.00	5.7	0.0	205.2	78.1	270.8	398.0	∞	∞	167.0
150	0.54	73	1.077	1667	0.00	5.4	0.0	196.4	74.3	279.4	401.5	∞	∞	161.0
160	0.54	70	1.079	1667	0.00	5.2	0.0	187.6	69.8	288.0	405.8	∞	∞	172.0

*HMK: Calculations based on the C_f -Re relationship of Hamana, Matsui and Kato.

**Sakiadis: Calculations based on the Sakiadis analysis of aerodynamic drag.

TABLE 16

EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6 ISOTHERMAL SPINNING
 TAKE-UP SPEED = 200 MET/MIN, TAKE-UP TENSION = 215.6 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	F _{rheo} dynes	Elongational Viscosity Poise x 10 ⁻⁴
1.5	7.85	8.8	--	247	--
3.5	7.29	10.2	1.07	245	5.48
5.5	6.51	12.8	1.74	243	4.19
7.5	5.68	16.8	2.15	241	4.41
9.5	4.99	21.8	2.63	239	4.66
11.5	4.47	27.2	3.15	238	4.81
13.5	3.98	34.2	3.69	237	5.14

TABLE 17

EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6 ISOTHERMAL SPINNING
 TAKE-UP SPEED = 300 MET/MIN, TAKE-UP TENSION = 264.6 DYNES

Distance from Spinneret cm	Fiber Diameter cm x 10 ²	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	F _{rheo} dynes	Elongational Viscosity Poise x 10 ⁻⁴
1.5	7.85	8.8	--	265	--
3.5	7.02	11.0	1.55	263	4.38
5.5	6.14	14.4	1.93	261	4.57
7.5	5.40	18.6	2.33	259	4.85
9.5	4.77	23.8	2.68	257	5.36
11.5	4.28	29.6	2.91	256	6.11
13.5	3.83	37.0	4.07	255	5.45

TABLE 18

EXPERIMENTAL AND CALCULATED DATA FOR NYLON-6 ISOTHERMAL SPINNING
 TAKE-UP SPEED = 556 MET/MIN, TAKE-UP TENSION = 343 DYNES

Distance from Spinneret cm	Fiber Diameter cm. x 10^2	Fiber Velocity cm/sec	Velocity Gradient sec ⁻¹	F _{rheo} dynes	Elongational Viscosity Poise x 10^{-4}
1.5	7.85	8.8	--	280	--
3.5	6.72	12.0	1.96	278	4.00
5.5	5.73	16.5	2.35	276	4.55
7.5	5.01	21.6	2.59	274	5.37
9.5	4.48	27.0	2.93	272	5.88
11.5	4.03	33.4	3.81	271	5.56
13.5	3.59	42.2	4.38	270	6.10

TABLE 19

PROPERTIES OF SPUN NYLON-6 FIBERS CONDITIONED
AT 65 PERCENT RELATIVE HUMIDITY AND 20°C FOR 24 HOURS

Take-Up Velocity met/min	Spline Stress dynes/cm ² x10 ⁻⁶	Tensile Properties			Birefringence x10 ³	Orientation Factors	
		Tensile Strength dynes/cm ² x10 ⁻⁹	Modulus dynes/cm ² x10 ⁻⁹	Elongation to Break percent		f _a	f _c
100	0.63	1.27	3.93	750	1.1	-0.1892	0.3784
200	1.84	1.27	4.09	630	4.5	-0.2853	0.5706
300	3.62	1.46	3.96	650	7.0	-0.2988	0.5976
556	8.89	1.51	3.95	510	15.0	-0.3428	0.6856
1000	20.50	2.09	4.04	240	22.8	-0.3172	0.6344
1500	37.80	2.89	5.20	104	26.7	-0.3437	0.6874
2000	--	3.72	--	64	28.6	--	--
2400	--	3.49	7.61	79	32.1	--	--

VITA

Vilas G. Bankar was born on November 26, 1946 in Bombay, India. After completing his high school education in 1963 from Union High School, Bombay, he attended the St. Xavier's College for one year and then entered the Indian Institute of Technology, Bombay, where he received a degree of Bachelor of Technology in chemical engineering in 1969.

Upon graduation, he worked as a production supervisor for Calico Chemicals and Plastics Company of Bombay for six months and as a production superintendent for Nirlon Synthetic Fibers and Chemicals Company for eighteen months.

In 1971, he entered the University of Akron, Akron, Ohio, and received an M.S. degree in chemical engineering. He entered the University of Tennessee, Knoxville, Tennessee in 1972, from where he received a Ph.D. in chemical engineering in 1976.

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