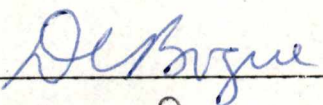
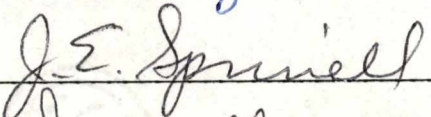
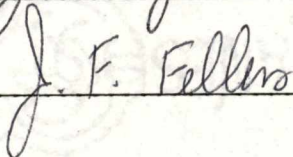


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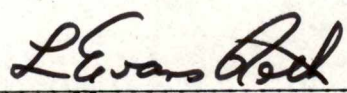
I am submitting herewith a thesis written by Fredson Boateng entitled "Processing History Induced Birefringence and the Mechanical Behavior of Anisotropic Filaments of Vitrified Polymethylmethacrylate and Polystyrene." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


James L. White, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:


Vice Chancellor
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PROCESSING HISTORY INDUCED BIREFRINGENCE AND THE MECHANICAL BEHAVIOR
OF ANISOTROPIC FILAMENTS OF VITRIFIED POLYMETHYLMETHACRYLATE
AND POLYSTYRENE

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Fredson Boateng

June 1980

3041733

DEDICATION

The author wishes to dedicate this work to his father, Mr. E. K. Boateng, whose untimely and tragic death occurred recently.

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude for the advice and guidance of Professors J. L. White and J. F. Fellers throughout this work. Appreciation is also expressed to Professor H. J. Johnson, Head of the Department of Chemical, Metallurgical and Polymer Engineering, the National Science Foundation and the Plastics Institute of America for supporting this work.

The author is particularly indebted to Professors White and Johnson for making it possible for him to attend The University of Tennessee, Knoxville. The assistance received from Al Carter, Mrs. Cagle, Gregory Caffey and the entire Chemical, Metallurgical and Polymer Engineering Department is fully appreciated. The help received from H. B. Thompson and Professor D. C. Bogue in equipment design is greatly appreciated.

Finally, to his uncle, Mr. D. K. Adom, his mother, Madam Yaa Nsiah, and his cousins Kwame Adom and Julie Sarpong, goes his deepest gratitude for their true concern and emotional support throughout the years.

ABSTRACT

The purpose of this experimental study was to investigate the processing history induced birefringence and the mechanical behavior of anisotropic filaments of vitrified polymethylmethacrylate and polystyrene. Oriented filaments have been prepared by melt spinning and by oven drawing. Analysis of the internal stresses in the filaments indicates that even though the overall birefringence is made up of contributions from molecular orientation and thermal stresses, the thermal stress contribution is relatively much greater in polymethylmethacrylate than in polystyrene. The non-linear birefringence-stress behavior obtained for polymethylmethacrylate is interpreted in terms of this significant effect of thermal stresses. This effect is greater in melt spinning than in oven drawing.

The mechanical properties of polymethylmethacrylate filaments at room temperature are obtained with 100% per minute strain rate. The modulus, yield stress and tensile strength all generally increase with birefringence, while the percent elongation-to-break initially increases to a point and then decreases showing a discontinuity at a birefringence of about -0.35×10^{-3} . The torsional modulus is little affected by birefringence, and no correlation is found between Poisson's ratio and birefringence. In general the mechanical properties are little or not affected by thermal stress.

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CHAPTER I

INTRODUCTION

The ability of vitrifying amorphous polymer melt, such as polymethylmethacrylate and polystyrene, to become highly birefringent through processing is well known. Such a phenomenon has been observed in melt-spun filaments (4,91), injection-molded parts (11,29,30,106,128), and in sheets and films (112,119). The birefringence so developed has been associated with molecular orientation (43,69,121). As has been pointed out by Wilkes (136), such molecular orientation resulting in molding operations may or may not be desired depending on the final use of the material. In general, however, flow-induced birefringence in most plastic parts results in mechanical anisotropy (52,129) and greatly modified performance characteristics (29,53,119,132). Similar studies have correlated these properties to the molecular orientation and its distribution (5,10, 53,89,107).

Glassy polymers possess other qualities that have attracted many researchers. They have unique combinations of optical clarity and desirable mechanical characteristics which fulfill many engineering design problems. They are easy to process, and by changing the processing conditions, their properties can be changed. The most common among these glassy polymers are polystyrene, polymethylmethacrylate, polyvinylchloride, polycarbonate, and esters of cellulose. Other glassy polymers include polyvinylacetate, the polysulphones, polyvinyl formals, polyvinyl carbazole, and the cross-linked polyesters. Polyethylene terephthalate can also be obtained as a non-crystalline polymer glass.

The present research is concerned with the properties of the flow history induced birefringence and the mechanical behavior of anisotropic filaments of vitrified polymethylmethacrylate and polystyrene prepared from two processing operations: melt-spinning and oven-drawing. Similar studies have been done on polystyrene in our own Laboratory (91), so the main effort will be focused on polymethylmethacrylate. However, there will be critical comparisons of the behavior and properties between the two glassy polymers.

CHAPTER II

BACKGROUND

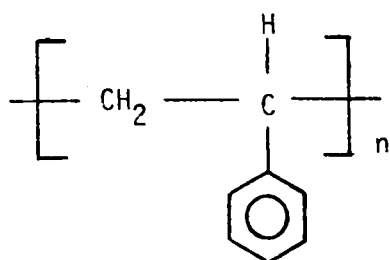
A. THE NATURE OF POLYMERIC GLASSES

Polymeric glasses comprise a class of plastic materials consisting essentially of long chain organic molecules having a disordered structure (14,50). Some polymers form glasses because of their low tacticity and others because of slow crystallization kinetics. Typical crystalline polymers are those whose molecules are chemically and geometrically regular in structure despite the fact that occasional irregularities, such as chain branching, can limit the extent of crystallization (14,50).

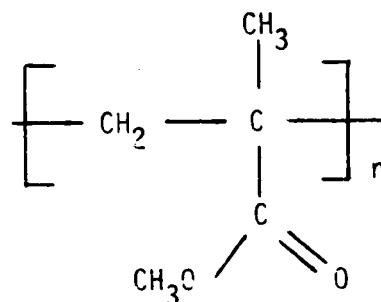
The long chain molecules of polymeric glasses usually contain single repeating monomer units joined by covalent bonds. However, some plastics are prepared as copolymers. Polymer samples of the same general type can be distinguished from each other by the magnitude and distributions of their molecular weights (50). The structural units of the major polymer glasses are represented in Figure 1. During manufacturing, stabilizers and lubricants can be added to glassy polymers to obtain useful combinations of properties.

Polymer glasses which consist of separate long chain molecules soften and flow under the influence of heat and are termed thermoplastic. Others contain a network of cross-links which allow them to soften at high temperatures but not to flow. Generally, it is believed that the introduction of cross-links into a polymer glass leads to increased brittleness (12,17). Evidently, the absence of crystallinity in typical

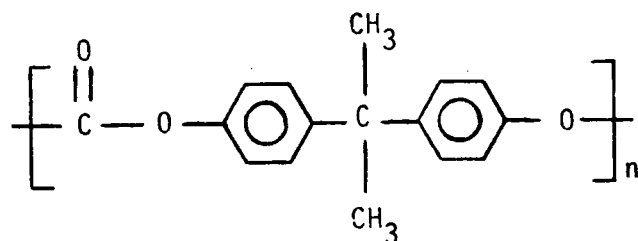
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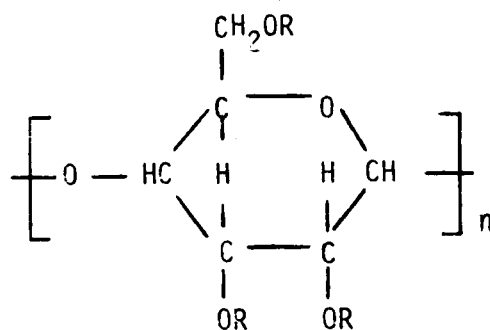
POLYMETHYLMETHACRYLATE



POLYCARBONATE



ESTERS OF CELLULOSE



POLYETHYLENE TEREPHTHALATE

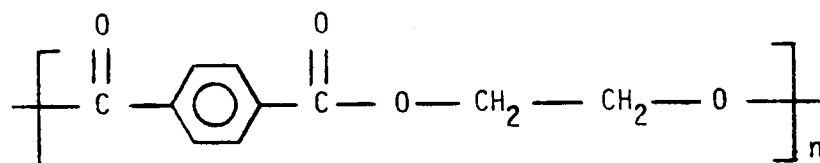


Figure 1: The Structural Units of the Major Polymer Glasses.

glassy polymers is due to the combination of their atactic structure and the size of their substituent groups (14).

B. STRUCTURE OF GLASSY POLYMERS

The attempts by several authors to totally explain the structure of glassy polymers have so far not been fruitful. There is a lot of controversy on this subject, and until now nobody has come up with a model or explanation that is acceptable. Zachmann (141) has critically reviewed the various theories and models that have been proposed, and all point to the various types of structural heterogeneities in molten and glassy polymers. These are characterized by: 1) short-range order, 2) bundles of chains, 3) small unstable crystals (heterogenous), and 4) special structures occurring only in the glassy state.

The chain bundles concept has attracted considerable attention, and several models have been proposed. Yeh (138) has proposed the model of bundles with chain folding. Also, Yeh and Geil (137) have used electron microscopy on PET and PC, and they claimed that they found small balls which were visible in the dark field and these indicated bundles. Zachmann (139,140) has achieved similar results on molten polyethylene using the Nuclear Magnetic Resonance method. Electron diffraction studies on PET indicated that if bundles exist, they show no sharply distinctive intermolecular distances (126). Light scattering on PMMA (35) has also shown that if bundles exist, they must have a very small anisotropy. Lastly, neutron scattering on PMMA and molten polyethylene (138) has shown that if bundles exist, the radius of gyration of a chain must be the same as for randomly coiled chains.

C. PHYSICAL AGING

When a polymer, initially in the molten state, is cooled to below glass transition temperature, T_g it is no longer in thermodynamic equilibrium. Its volume, entropy, etc., being too large, it slowly begins to approach the equilibrium state, a process which causes many properties of the material to change with time. This phenomena is the so-called physical aging. According to Struik (117,118), this physical aging can be considered to be caused by a hydrostatic internal stress which, by a process of bulk creep, produces a slow and gradual contraction of the material.

It has been known for more than a generation that amorphous materials are not in thermodynamic equilibrium at temperatures below their glass transition. Kovac's volume relaxation studies (68) reveal that below T_g the molecular mobility is not quite zero. There have been several studies on this aging process (67,87,116) which indicate that during aging, plastic materials become stiffer and more brittle, and their damping, creep, and stress-relaxation rates decrease.

The basic aspects of physical aging in amorphous polymers are well known (117). Firstly, aging in general occurs in broad temperature ranges below T_g , running from T_g down to the first secondary transition, T_β . Secondly, the small-strain mechanical properties are determined mainly by the parameter aging time and by the fact that the prediction of long-term behavior should include the effect of aging. Thirdly, in the aging range, all polymers age in the same way, and even their mechanical behavior at small strains is very similar. Lastly, aging is thermoreversible, and it does not affect secondary relaxations. Studies (68,116)

have indicated that both aging and glass transition can be explained using free volume concept. It would appear that aging is a basic feature of the glassy state found in all glasses irrespective of their specific chemical, polymeric, or monomeric structure.

D. RESIDUAL THERMAL STRESSES

Products of amorphous polymers are usually made by deformation of the material in the molten or rubbery state and subsequent fixation of the desired shape by cooling to below the glass transition temperature, T_g , with this cooling being rapid. As a result of this, different kinds of internal stresses are introduced in the finished product. One of these internal stresses is the thermal stress.

Thermal stresses are the result of rapid cooling to below T_g . Because the material is cooled from its surface inwards, rapid cooling is inherently inhomogeneous, and the resulting volumetric strains bring about thermal stresses (118). The elastic properties of the polymer change during cooling, and part of these thermal stresses will persist when the cooling has been completed. Thus, in a quenching of a molten cylinder, it cools rapidly from the melt temperature to room temperature. Vitrification occurs first in the outer radii and fixes the diameter of the cylinder and its average density. As cooling continues radially inwards, the equilibrium density of the internal molten core is at any instant lower than the average density fixed by the outer layers of the cylinder. This sets up an internal stress field, with the outer layers being under compression and the inner core in a state of residual tension. Production of such thermal stresses has been known since the time of Brewster (20) to give rise to birefringence (22,100,105,118).

The methods of analysis of thermal stresses have been presented in terms of linear elasticity by numerous authors dating back to Maxwell (84) and Rayleigh (100) and reviewed by Timoshenko and Goodier (120) and Boley and Weiner (15). All these analyses invariably involve inorganic glasses and metallic parts of different geometric shapes, and none involve plastics. The thermoelastic analysis for an infinitely long solid circular cylinder has been worked out by these authors, and the solution is essentially given as (15,100,120):

$$\sigma_{rr} = \frac{2G\alpha(\lambda + \frac{2}{3}G)}{(\lambda + 2G)} \left[\frac{1}{r^2} \int_r^R \theta r \, dr \right] \quad (\text{II-1a})$$

$$\sigma_{\theta\theta} = \frac{2G\alpha(\lambda + \frac{2}{3}G)}{(\lambda + 2G)} \left[\frac{1}{r^2} \int_r^R \theta r \, dr - \theta \right] \quad (\text{II-1b})$$

where λ and G are Lamé's constants, α is the coefficient of thermal expansion, and θ is the temperature difference between the body and the surroundings. The principal assumptions underlying the analysis are: the temperature can be determined independently of the deformations of the body; the deformations are small; and the material behaves elastically at all times.

The thermoelastic analysis has some shortcomings; it assumes linear elasticity with constant elastic properties and that the temperature changes should also be small. Some modifications are needed to take into consideration the non-linear viscoelastic and plastic behavior of polymers, and also large temperature changes during processes such as melt-spinning.

Thermal stresses play an important part in fabrication of polymer parts (21,107). Broutman et al. (22) and Petrie and her co-workers (93)

have determined residual thermal stresses having maximum values up to 2.07×10^8 dynes/cm² in compression at the polycarbonate sheet surface using birefringence measurement techniques. These authors have also shown these thermal stresses improve the impact behavior, in addition to having beneficial effects on aging. Struik (118) has determined thermal stresses as high as $1 - 2 \times 10^8$ dynes/cm² in PMMA sheets quenched in oil.

E. ORIENTATION

General

(Orientation in polymer systems is generally defined as a preferential alignment of polymer chains in specific directions. The lined up molecules, which have different characteristics parallel and perpendicular to their long dimensions, give an anisotropic behavior to many physical properties (45,89).) Studies have shown that orientation plays an important role in the control of physical properties of polymers (23,25,29,30, 34,52,53,58,98,99,108,123,129,132).

Molecular orientation occurs inevitably in most mechanical fabrication operations, and its effects can be either favorable or unfavorable, depending on the directions of orientation relative to the stresses encountered in service (2,136). Orientation has been characterized in many ways, the most common being the specification of uniaxial orientation, as in samples with fiber orientation, by the orientation function f , popularly known as Herman's orientation function (51).

Measurement of Orientation

(The degree of orientation in polymers can be measured by various techniques. The measurement is complicated both by the complexity of

the types of orientation which can occur and by the conceptual difficulties involved in the current picture of the structure of an oriented specimen (14). Stein and Read (113) have written a critical assessment of the methods for the determination of orientation in amorphous polymers.

In principle, molecular orientation in amorphous polymers can be determined using x-ray diffraction (14,50). The method involves analysis of the intensity distribution of the scattering in the amorphous halo in the diffraction pattern. This method is seldom used due to experimental difficulties. It is, however, very useful in crystalline and semi-crystalline polymers (51,111).

Infra-red dichroism is another technique. Since infra-red absorption is dependent upon changes in dipole moment, this method can pick up changes in the orientation of selected groups in the polymer (71). The difficulties with this technique are that it has only limited sensitivity at small degrees of orientation, and also the sample has to be extremely thin (18).

Broad-line nuclear magnetic resonance (NMR) adsorption has been used to obtain orientation functions for oriented amorphous and crystalline polymers, but so far only for high degrees of orientation (63). The method is a development of that previously used for semi-crystalline polymers and demands high accuracy in the determination of the second moments of the NMR adsorption signal (85).

Laser Raman scattering from polymethylmethacrylate (96) and polyethylene terephthalate (97) have confirmed that Raman technique is capable of giving quantitative information about molecular orientation in polymers. This technique demands that corrections have to be made for the

birefringence effects resulting from the refractive index of the sample, especially if it is highly oriented (97).

Birefringence is the easiest and the most common technique for measuring orientation in amorphous polymers (18,31,72,136). Birefringence can be defined as the difference in the refractive indices of two perpendicular directions as measured with light polarized along these respective directions (136). Molecular orientation will in general give rise to non-zero birefringence. The measurement of how the birefringence changes with respect to a reference axis gives an indication of how the molecular chains are orienting. There are, in general, three birefringences, two values of which are independent (136):

$$\Delta_{xy} = n_x - n_y \quad (\text{II-2a})$$

$$\Delta_{yz} = n_y - n_z \quad (\text{II-2b})$$

$$\Delta_{xz} = n_x - n_z = \Delta_{xy} + \Delta_{yz} \quad (\text{II-2c})$$

The basis of the molecular theory of orientation induced birefringence is as follows: Since polymer chains possess different polarizabilities α_1 and α_2 along and perpendicular to the backbone, it follows from the theory of dielectrics that an oriented polymeric medium will have direction-dependent dielectric constants, and from the electromagnetic theory of light that the refractive index will have a similar dependence (16,82). Thus, in a uniaxially oriented filament with birefringence, $\Delta n = n_{11} - n_{\perp}$, the level of orientation can be represented by the Herman's orientation factor (51,142):

$$f_H = \frac{\overline{\alpha_{11} - \alpha_{\perp}}}{\alpha_1 - \alpha_2} \quad (\text{II-3})$$

where α represents the molecular polarizability and subscripts 1 and 2 represent the directions along and perpendicular to a polymeric chain, respectively. The birefringence may then be shown to be, according to dielectric and electromagnetic theory (43,109):

$$\Delta_n = \frac{2}{9} \pi \cdot \frac{N\rho}{M} \cdot \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot (\overline{\alpha_{11} - \alpha_{\perp}}) \quad (\text{II-4})$$

$$= \Delta^{\circ} \cdot f \quad (\text{II-5})$$

where

$\bar{n}$ = average of n_{11} and $n_{\perp}$

Δ° = maximum or intrinsic birefringence of the system; i.e.,

$$\Delta^{\circ} = \frac{2}{9} \pi \cdot \frac{N\rho}{M} \cdot \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \cdot (\alpha_1 - \alpha_2) \quad (\text{II-6})$$

Thus, if Δ_n , $\bar{n}$, $\frac{N\rho}{M}$, and $(\alpha_1 - \alpha_2)$ are known, f can be calculated.

F. CONSEQUENCES OF MOLECULAR ORIENTATION

Due to the thermomechanical history (deformation above T_g), a state of molecular orientation is frozen in. This orientation results in anisotropy in the physical properties of the material. The anisotropy is a purely geometrical consequence of the state of molecular orientation (118).

Thermal twisting studies on PC, PS, and PMMA (118), whereby a high twist is given to a polymer rod at a temperature above T_g , and is frozen-in

by cooling down to room temperature, have demonstrated that lowering of temperature increases the twist. This phenomenon has been explained to be a direct consequence of the inherent rubberlike elasticity of the oriented molecules (123).

Dimensional instability is another property of frozen-in molecular orientation. It is clearly demonstrated by shrinkage measurements in which the changes in dimension that take place when an oriented specimen is heated to above its softening point are measured. Such a technique has been used to study orientation distribution in injection molded parts (86). Jones (58) has shown with polystyrene sheets that the more the sample is oriented, the higher the shrinkage. The dimensional instability has been attributed to the delayed response of the viscoelastic polymer to the stresses imposed on it during processing (118).

Studies with PC and PVC (118) have shown that frozen-in uniaxial orientation gives a negative contribution to the linear thermal expansivity measured in the stretching direction. Similar results have been obtained for semi-crystalline polymers (26). This negative contribution is believed to be due to the lower expansivity of the stiff bonds in the chain direction and the temperature-dependence of the frozen-in entropic stress (118,123).

Fracture properties of oriented PMMA and PS have been studied by Curtis (33) using cleavage method. The study shows that crack propagation parallel to the direction of orientation is much easier than in the transverse direction, and that in a tensile test there is the tendency for the sample to fail by multiple lengthwise splitting or fibrillation rather than by direct transverse fracture. Doyle (37) has observed similar crack propagation behavior in oriented PS.

G. ORIENTATION IN FLOWING POLYMER MELTS

Investigation into the relationship between orientation development and flow started a long time ago with Maxwell's studies into induced birefringence in flowing fluids (83). Subsequent researches involving flow birefringence in polymer solutions are contained in a review by Edsall (38). Similar studies have been carried out showing birefringence in flowing polymer melts (1,39,40,45,46,47,55,127).

The modern research perspective on flow birefringence which is based on the rheo-optical law was developed by Lodge (75) in 1956. This author realized the similarity between vulcanized rubber and concentrated polymer solutions and melts with regard to their molecular structure and deformation mechanisms, and hypothesized that similar relationships should exist between birefringence and stress. Philippoff (95) was among the various researchers who experimentally verified this hypothesis.

The stress-birefringence theory has recently been applied to flowing polymer melts (40,45-48,78,91,127), and most of these studies have been for steady-state shear flow. Studies by Janeschitz-Kriegl et al. show the validity of stress birefringence theory for the transient shear flow of polymer melts, while those of Matsumoto and Bogue (78) and Oda, White, and Clark (91) show the validity of the rheo-optical laws for polymer melts in uniaxial extension.

From phenomenological viewpoint, the rheo-optical law essentially states that: the refractive index and stress ellipsoids are coaxial and that the birefringence (difference in magnitude of the principal axes of the refractive index ellipsoid) is proportional to the corresponding difference in principal stresses. Specifically (56,57,81,110,114,121,122):

$$n_i - n_j = C(\sigma_i - \sigma_j) \quad (\text{II-7a})$$

or

$$\underline{n} - n_o \underline{I} = C(\underline{\sigma} - \sigma_o \underline{I}) \quad (\text{II-7b})$$

where

$$n_o = \frac{1}{3} \text{tr } \underline{n} \quad \sigma_o = \frac{1}{3} \text{tr } \underline{\sigma} \quad (\text{II-7c})$$

with $\underline{n}$ the refractive index tensor, $\underline{\sigma}$ the stress tensor, $\underline{I}$ the identity matrix, and C the stress-optical coefficient. Thus, in the melt-spinning of a fiber or elongation of a filament of radius R under tension F ,

$$\begin{aligned} \Delta n &= C(\sigma_1 - \sigma_2) = C\sigma_1 \Big|_{\text{vitrification}} \\ &= C\left(\frac{F}{\pi R^2}\right) \end{aligned} \quad (\text{II-8})$$

where 1 refers to spinline (axial) direction, and 2 refers to radial direction.

From equations (II-5) and (II-8), one obtains

$$\begin{aligned} \Delta^\circ \cdot f &= C\sigma \\ f &= \frac{C}{\Delta^\circ} \cdot \sigma \end{aligned} \quad (\text{II-9})$$

In shear flow, the stress-optical law implies that the angle χ between the flow direction and the principal axes of the stress tensor is the same as the optical extinction angle χ_{opt} , and

$$\begin{aligned}
 \Delta n &= \frac{C(\sigma_{11} - \sigma_{22})}{\cos 2\chi_{\text{opt}}} \\
 &= \frac{2C\sigma_{12}}{\sin 2\chi_{\text{opt}}} \\
 &= C[(\sigma_{11} - \sigma_{22})^2 + 4\sigma_{12}^2]^{\frac{1}{2}} \quad (\text{II-10})
 \end{aligned}$$

where 1 refers to flow direction, and 2 refers to the shear direction.

H. ORIENTATION DEVELOPMENT IN VITRIFYING POLYMER MELTS

In many polymer processes, flowing and stressed melts are cooled and vitrified. The orientation frozen-in by vitrification during or following flow may be related to the stress field existing during flow. Oda, White, and Clark (91) have shown that birefringence distributions developed in polystyrene during elongational and shear flow are frozen in during vitrification. These authors point out that the rheo-optical laws applicable in the melt may be used to determine birefringence distributions in the vitrified polystyrene. This phenomenon has been found to apply in the case of amorphous polyethylene terephthalate (94). The method has been used by Dietz, White, and Clark (36) to predict orientation distributions in injection-molded parts.

Another characteristic behavior of vitrifying polymers is that, due to finite cooling rate through a filament following a hot drawing operation, a radial distribution in birefringence results. Such radial birefringence variations in vitrified polystyrene filaments have been described by Gurnee (43) and Andrews (4). The former has analyzed this problem mathematically by considering the birefringence at any point

along the radius of the filament to be proportional to a distribution function, $D(r)$. The analysis essentially yields

$$\Gamma_{zx} = 2 \int_r^R (r^2 - a^2)^{-1/2} D(r) r dr \quad (\text{II-11})$$

where Γ_{zx} is the total retardation through the vertical path in the ZY plane at the distance "a" from the center, x is the direction of filament axis, r is any point along the radius vector, and R is the filament radius. Gurnee (43) has further obtained $D(r)$ experimentally by the "wedge method." The expression relating the retardation to the distribution function is:

$$D(y) = \cot \theta (d\Gamma_{zx}/dz) \quad (\text{II-12})$$

where the variable y replaces r to avoid ambiguity, and θ is the angle the cut surface makes with filament axis. Expression (II-12) thus maps out the birefringence across the filament diameter.

I. THE RHEO-OPTICAL BEHAVIOR OF VITRIFYING POLYMERS

As stated earlier, vitrifying polymer melts exhibit optical anisotropy through processing. This optical anisotropy is believed to be a consequence of mechanical anisotropy resulting from deformation (3). Some of the experimental conditions used in studying rheo-optical behavior of polymers include conditions of vibrational strain, steady-state deformation, relaxation, and creep. Rheo-optical studies have helped in investigating the molecular mechanism of mechanical relaxation in polymers (101,102).

The stress-birefringence relationship for some vitrifying polymer melts has been known to be affected by temperature changes. Robinson et al. (103), Read (102), and Tsvetkov and Verkhovina (125) have shown that the stress-optical coefficient of PMMA varies markedly with temperature. The latter authors' study shows that the stress-optical coefficient is positive at temperatures above 150°C and negative below this temperature, with the value reaching the negative maximum immediately above T_g . A study by Read (102) indicates that between temperatures of -130°C and 50°C, the temperature effect is very slight, but from 50°C to 100°C, absolute of the stress-optical coefficient increases gradually. This author attributes the increase to β relaxation.

It has been shown for PS that the stress-optical coefficient is small and positive at temperatures below T_g (58,64,66,104), and large and negative in the rubbery state above T_g (58,64,78,89,91). Stress-relaxation studies (44) indicate that in the neighborhood of T_g the change of the stress-optical coefficient from positive to negative is very sharp. It is explained (104) that the positive value in the glassy state is due to the alignment of phenyl groups in the direction of applied stress, while the negative value is due to the alignment of polymer chains in the direction of applied stress, thus compelling the plane of the phenyl groups to be aligned perpendicular to this direction. The large negative stress-optical coefficient in the melt allows birefringence to be frozen-in during vitrification (4,91).

Nobbs and co-workers (90) and Pinnock and Ward (94) have indicated that for temperatures below 100°C, the stress-optical coefficient of amorphous PET is essentially constant. These authors noted that at higher temperatures there is the possibility of crystallization taking place.

Studies have also shown that the frozen-in birefringence varies with temperature in polymers like PMMA and PVC (7,118) and PET (94). The frozen-in birefringence decreases in magnitude as the temperature increases. On the other hand, in polymers such as PC (118) and PS (7,118), the effect is negligibly small. It is explained that the higher the ratio of the stress-optical coefficients of the glass and the rubber, the greater the temperature dependence of the frozen-in birefringence (118). In PS, the lack of temperature dependence on frozen-in birefringence has been attributed to the rigidity of the phenyl ring and its lack of rotation about the connecting bond to the chain (7). This author attributes the greater temperature dependence of the frozen-in birefringence in PMMA to the greater mobility of the non-rigid ester side group. Other studies (102, 125) have shown that in PMMA, the conformation of the ester group, and consequently its anisotropy, depends on the state of internal rotation about the C-C and C-O bonds in the ester group. The appreciable change of orientation birefringence with temperature, especially in the glassy state, thus strongly argues for the existence of a significant degree of molecular motion in the glassy state, in contrast to the concept of a glassy polymer as a totally frozen structure.

The variations of stress-optical coefficient with temperature for PMMA, PS, and some other polymers are shown in Appendix A.

J. MECHANICAL PROPERTIES OF ORIENTED GLASSY POLYMERS

(The mechanical performance of a thermoplastic article depends upon the molecular structure (largely established during polymerization) and the spatial arrangement of the molecules (established by the fabrication

process). This latter aspect of structure includes molecular orientation in amorphous polymers, morphology and orientation in crystalline polymers, and geometrical disposition of the phases in multiphase materials such as composites and foams (2).

Mechanical properties of polymeric glasses and performance characteristics of products produced from them have been found to be greatly influenced by the molecular orientation and its distributions (5,10,29,30, 53,89,107). In general, unoriented glassy polymers at room temperature are brittle, glassy, amorphous polymers. However, uniaxially oriented glassy polymers are highly anisotropic. In the direction of orientation they can have a high tensile strength and ductile extensibility, and resistance to environmental stress-crazing (132) and stress-cracking (58). However, in the transverse direction they are even weaker and more susceptible to stress-crazing than unoriented specimens. The tensile strength in the orientation direction increases with increasing level of orientation (89), while the elongation-to-break rises to a maximum and then decreases (60,61).)

The study of Nielsen and Buchdahl (89) on polystyrene films indicates that, in general, the value of the stress-strain properties in the direction of hot stretch, the dynamic modulus, and the birefringence all increase with an increase in the amount of stretching. Studies on injection-molded polymers (46) have shown that the ultimate properties of the molded specimen depend on the microstructure developed in the molding process, and such specimens possess anisotropic mechanical and optical properties. Jones (58) has shown increasing orientation in polystyrene improves rupture stress, rupture strain, specific rupture energy, and impact strength.

Recently, Spruiell, White, and co-workers (88), too, have studied melt-spinning of crystalline polymers, and their findings indicate that the mechanical properties, such as modulus, yield strength, tensile strength, and elongation-to-break, all correlate with spinline stress, which in turn correlates with both orientation and birefringence. These authors have specifically shown that polypropylene filaments melt-spun under low stress conditions usually exhibit a yield drop and necking elongation, in contrast to less prominent necking in those spun under higher spinline stresses; the yield and tensile strength and the modulus all increase with spinline stress in contrast to percent elongation, which decreases with increasing spinline stress. It has previously been shown by Dees and Spruiell (34) that as spinline stress increases, the greater molecular orientation developed in the molten state in spun fibers leads to increases in modulus and tensile strength.)

It must be pointed out that in the study of tensile strength of oriented polymers, two main difficulties are encountered (123). Firstly, the strength is extremely sensitive to minor surface defects and structural inhomogeneities which give rise to local stress concentrations. Secondly, the actual process of testing may produce a modification of the original orientation which may be very considerable.

Another important property of glassy plastics from the practical standpoint is the softening temperature. This gives an indication of the temperature range where the material goes through a transition from a hard, rigid substance to a soft, rubbery one. It has been demonstrated with oriented polystyrene sheets (89) that the softening temperature is lowered with increasing birefringence.

K. MECHANISM OF DEFORMATION AND FRACTURE IN GLASSY POLYMERS

Treloar (123) has suggested that in order to understand the effects of molecular orientation in polymers, it is necessary to examine the way in which the properties of any given material are determined by its molecular structure and by the bonding mechanism whereby the molecules are held together. In glassy polymers, the forces between the long-chain molecules (Van der Waals forces) are relatively weak, and deformation takes place mainly by separation of chains or by limited rotation about bonds within the chain, rather than by deformation of the primary chemical bonds within the chain itself. This author has examined the fracture properties of glassy polymers and has concluded that the fracture process does not correspond to a simple separation of two planes of atoms, as envisaged in the classical treatment, but must involve extensive local breakdown of the structure or other dissipative processes. Such processes are revealed by the phenomenon of crazing and by the formation of visible films on the fracture surface.

Kambour and Robertson (59) have made a very critical analysis of behavior of plastics. At low stresses, the plastic strains very nearly elastically, while at high stresses, the plastic can exhibit either the ductile response, involving yielding and flow, or the brittle response involving crazing and fracture. Which of the two, the ductile or the brittle response, actually occurs with a given material depends essentially on which response occurs most easily, i.e., which occurs at a smaller stress. This, in turn, depends on the conditions of the deformation. Three of the most common variables making up the conditions of the deformation are the strain rate, the temperature, and the stress configuration.

The higher the imposed strain rate, the more likely will the plastic be brittle. For a given temperature and stress configuration, there probably exists a critical rate above which a particular plastic is brittle and below which it is ductile. In general, the higher the temperature, the more likely will the plastic be ductile. However, for a given rate and stress configuration, there exists a critical temperature above which the plastic is ductile and below which it is brittle. For example, in tension at a strain rate of 0.003 sec^{-1} , the critical temperature is about 85°C for polystyrene, 50°C for polymethylmethacrylate, and -100°C for bisphenol-A polycarbonate (59). It is also known that the larger the shear component in the applied stress relative to the tensile component, the more likely will the plastic be ductile (59). Crazeing and fracture are responses to a tensile stress, while yielding and flow are responses to a shear stress.

Some correlations between the intrinsic ductility and other measurable properties have been found. A review by Boyer (19) shows that ductility correlates with the existence of a large low-temperature loss peak. Bisphenol-A polycarbonate and polyvinylchloride have large low-temperature loss peaks and are ductile. On the other hand, polystyrene and polymethylmethacrylate do not have low-temperature loss peaks and are brittle. Another correlation is between the intrinsic ductility of glassy plastics and the "maximum fractional unoccupied volume" (MFUV), which is defined as the difference in specific volumes of the glass and the crystal (73). Bisphenol-A polycarbonate is ductile in tension at room temperature and has relatively large MFUV. Polystyrene is brittle and has a relatively small MFUV. However, polymethylmethacrylate has a

smaller MFUV than polystyrene, yet is intrinsically more ductile. This discrepancy has been attributed to the fact that the polymethylmethacrylate crystal may be inefficiently packed and that the true MFUV may be larger than that computed by subtracting the volume of the crystal.

Bucknall et al. (24) have studied the deformation and fracture in polymethylmethacrylate. At sufficiently high test temperature, well above the glass transition, individual molecules can move past each other; specimens deform at low stresses in a liquid-like manner. As the temperature is reduced, the forces between the molecules increase, and specimens become less easy to deform. At 130°C, polymethylmethacrylate is just above its glass transition, and it extends uniformly like a rubber. At 100°C, it is just below its glass transition, and a specimen of sufficiently high molecular weight yields, necks, and cold-draws.

Below the glass transition, at least three mechanisms of deformation can be distinguished in PMMA, in addition to uniform viscoelastic deformation (24):

1. Generalized plastic deformation. This takes place essentially at constant volume.
2. Formation of shear bands at approximately 45° to the applied stress. There is a small initial volume increase, which decays with time.
3. Formation of craze bands, or crazes, at right angles to the applied stress. There is a major increase in volume.

During tensile testing, mechanisms 1 and 2 lead to a macroscopic reduction in cross-sectional area, with a consequent general increase in

true stress, whereas mechanism 3 leaves the external cross-section virtually unchanged and results in high stresses in the oriented fibrils within the craze. Fracture of PMMA usually proceeds through the formation and rupture of a craze. All three mechanisms operate more rapidly with increase in tensile stress. At high stresses, the dominant factor is the increased rate of craze rupture, which gives rise to early brittle failure, with the other mechanisms having little time to contribute significantly to the deformation.

Molecular orientation along the axis of the tensile specimen inhibits all deformation mechanisms because they involve the rotation of chain segments toward this axis and are pre-empted by prior orientation. Both stiffness and strength increase with orientation; at high orientations crazing is completely suppressed, so that fracture proceeds by bond rupture in the bulk polymer (24).

L. DEGRADATION OF POLYMETHYLMETHACRYLATE

Polymethylmethacrylate degrades thermally by the process of chain depolymerization (14,28). Polystyrene degrades by the same process, but its monomer yield is much lower than that of polymethylmethacrylate because of side reactions in polystyrene. The factors which appear to determine the course of degradation are the reactivity of the depropagating radical and the availability of reactive hydrogen atoms for transfer. With the possible exception of styrene, where the radical is stabilized by resonance, all polymers containing α -hydrogens, such as polyacrylates and polyacrylonitrile, give poor yields on monomer. On the other hand, polymethylmethacrylate gives high yields of monomer

because of the active radical and the α -methyl group which blocks the possibility of chain transfer (25).

Wen et al. (131) have used thermogravimetric analysis to show that thermal degradation process of polymethylmethacrylate is of a simple first-order kinetic, and that the weight loss kinetics can be expressed by the equation:

$$K_1 = 5.3 \times 10^6 \exp \left(\frac{23,000 \pm 1,055}{RT} \right) \quad (\text{II-13})$$

where K_1 is the first-order rate constant in sec^{-1} , R is the gas constant, and T is temperature in kelvins. These authors also found that the degradation of polymethylmethacrylate starts around the temperature of 210°C .

According to Crawford (32), polymethylmethacrylate gives monomer as the principal volatile product of thermal degradation at temperatures up to 250°C . Grassie (41) maintains that polymethylmethacrylate cannot undergo an ester decomposition process because it does not contain β -hydrogen atoms. This author explains that decomposition of carboxylic acid esters to give acid and olefin proceeds by a molecular mechanism involving six-membered ring transition state and is clearly governed by the strength of the interaction which can occur between the carbonyl group and β -hydrogen atoms.

At high processing temperatures and high stresses, the possibility exists that damage to the molecular structure can occur via both thermal and mechanical degradation. Grayson et al. (42) show an equation for the rate of damage, as follows:

$$R = R_0 \exp - [(U_{ab} - \beta\sigma)/kT] \quad (\text{II-14})$$

where

R = rate of bond rupture in the polymer chain

R_0 = fundamental frequency factor

U_{ab} = activation energy for bond rupture

β = constant characteristic of the polymer

σ = applied stress

k = Boltzmann constant

T = temperature, °K.

CHAPTER III

EXPERIMENTAL STUDIES

A. MATERIALS

Two commercial resins were investigated in this research. These were:

1. Polymethylmethacrylate (Lucite 147K), a high molecular weight acrylic resin supplied by E.I. duPont de Nemours and Company.
2. Polystyrene (Dow Styron 678U), supplied by Dow Chemicals.

Both materials were in the form of pellets, with dimensions of about 3 mm x 3 mm x 3 mm. The polystyrene has been investigated in previous rheological and melt-processing studies in our Laboratories (91,133).

B. PREPARATION OF ORIENTED FILAMENTS

Two methods were used to prepare oriented filaments under known stress conditions. Both methods involve tensile elongation deformations. They include: 1) melt-spinning, and 2) oven-drawing at constant temperature.

Melt-Spinning

The melt-spinning process involved the use of an Instron capillary rheometer as a melt-delivery system. A capillary die with a diameter of 0.03 cm and a length of 1.00 cm was used. For each polymer, the pellets were vacuum-dried in an oven and were melt-extruded at specific temperatures. The filaments were taken-up with a variable speed control motor

(Bodine Elec. Co.) with a take-up roll. Varying oriented filaments were obtained by changing the take-up speed. The tensions in the Lucite 147K (PMMA) filaments during the melt-spinning process were measured using a Rothschild tensiometer with a 10-g measuring range. The experimental conditions used in the above process are summarized in Table I.

TABLE I
EXPERIMENTAL CONDITIONS

Sample	Spinning Temperature (°C)	Flow Rate ($\times 10^4$ cm ³ /sec)	Cooling Medium
Polymethylmethacrylate (PMMA)	180	8.3	Air
	190	8.3	Air
	200	8.3	Air
	220	8.3	Air
Polystyrene (PS)	180	8.3	Air

On-Line Measurements

On-line measurements of birefringence were made during the melt-spinning of PMMA for extrusion temperatures of 190°C, 200°C, and 220°C. These measurements were made with an Olympus polarizing microscope and a Berek compensator. The microscope was appropriately mounted so as to observe the running threadline. Similar measurements have previously been done on PS in our Laboratory (91). In the present study, the geometry

of the experimental set-up precluded measurements very close to the spinneret where the threadline was still molten.

On-line temperature measurements were also made along the threadline with a Hastings Match-Temperature Pyrometer. These measurements were done on PMMA at melt-spinning temperatures of 190°C, 200°C, and 220°C.

Oven-Drawing

The samples used in this process were isotropic. Filaments were freely extruded from the Instron rheometer, after which they were annealed at 105°C for about two hours. This process was repeated until a constant minimum birefringence reading of about 0.002×10^{-3} was achieved in the filaments.

Drawing was carried out at temperatures ranging from 107°C to 120°C on an Instron Table Model 1122 tensile tester. A predetermined length of filament, 8 cm, was clamped between the Instron grips, and the entire length of the filament was surrounded by radiant heating chambers. These were the same heating chambers used by Matsui and Bogue (77), and the sketch is shown in Figure 2. Essentially, the radiant heaters focus the heat from nichrome coiled wires onto the filament. Circulating air stream helps establish a uniform temperature inside the chambers.

After the filament was heated up to the temperature of the chambers, it was then drawn at a constant crosshead speed to the desired length. The chambers were then opened and the drawn filament allowed to cool to room temperature. A buzzer attached to the crosshead sounded just before the crosshead reached the end of its travel. This was necessary because the chambers had to be opened at the appropriate time to avoid any unnecessary stress relaxation. Different initial drawing rates ranging

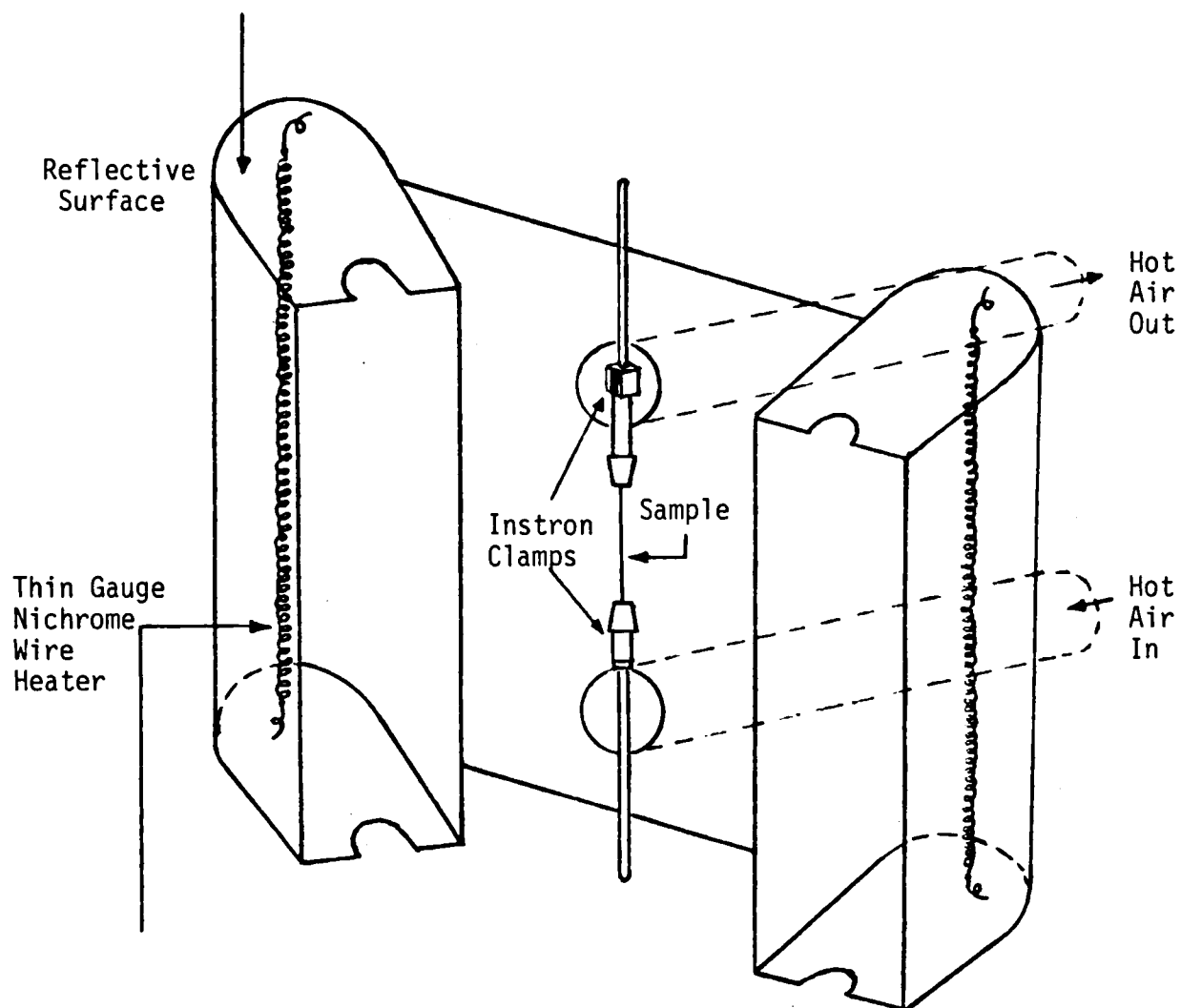


Figure 2: Sketch of Radiant Heating Chambers Shown in Open Position.

from 25-250% per minute and varying crosshead traveling distances were employed at each drawing temperature. Load-elongation curves were also recorded on the Instron chart. The deformation rate was defined as

$$\frac{\text{Crosshead speed in mm/min}}{\text{Gauge length in mm}} \times 100$$

Orientation Measurements

Birefringence is one of the best methods of measuring orientation in glassy polymers. The birefringence measurements of both the melt-spun and oven-drawn filaments were made using an Olympus polarized microscope with crossed polarizers and a Berek-type compensator. For highly oriented samples, the birefringence measurements were obtained using an Orthoplan polarizing light microscope with a Leitz compensator. The birefringence in each case was defined as the ratio of the measured phase difference (retardation) to the diameter of the filament. The diameters of the filaments were measured with a microscope fitted with a filar eyepiece which had been calibrated with a stage micrometer.

Temperature Dependence of Birefringence

The temperature dependence of birefringence was investigated by measuring the birefringence changes of an initially oriented filament under conditions of varying temperature. The set-up essentially consisted of a polarizing microscope with compensator, hot stage, and a temperature control device. The temperature range of the experiment was from 25°C to 80°C. The experiment was performed on oriented filament maintained at constant length (restricted length) and an oriented filament not restricted in length (unrestricted length). The device for maintaining length is sketched in Figure 3.

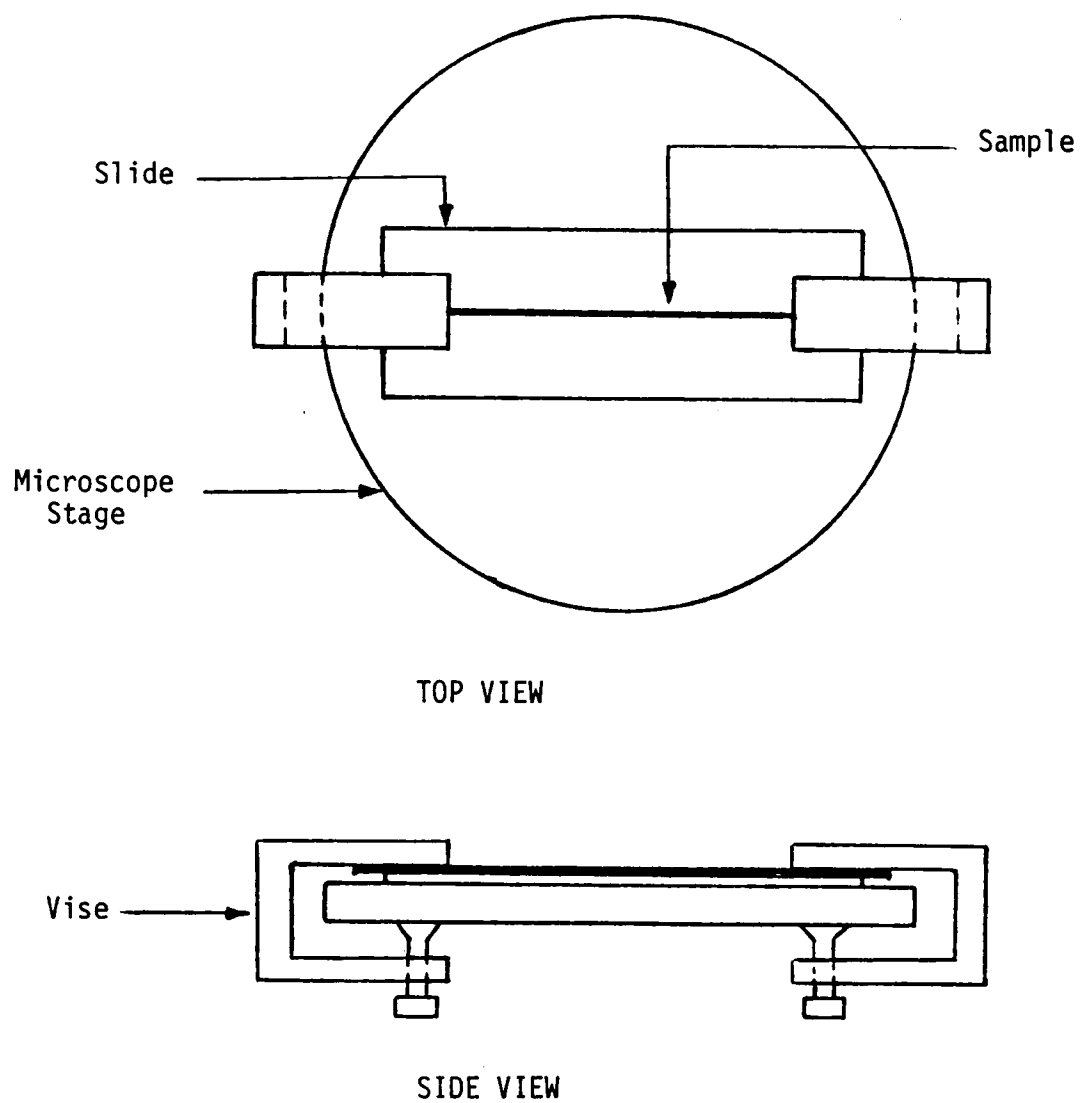


Figure 3: A Sketch of the Set-Up for Maintaining Constant Filament Length (i.e., Restricted Length).

Thermal Stress Birefringence

To investigate the effect of thermal stresses, freely extruded filaments of both PMMA and PS were placed in boiling water. They were then removed just before they were about to coil up and were quickly quenched in ice water bath to which some salt had been added. Birefringence measurements were made on these ice-quenched filaments.

In a parallel experiment, filaments were freely extruded without take-up device. The extrusion rates and temperatures were the same as shown in Table I. Different dies were used to obtain significant variety of diameters. Birefringence measurements were then made on these filaments.

Mechanical Properties

The stress-strain data were obtained on an Instron tensile tester (Table model 1122) using a crosshead speed of 20 mm/min and a specimen gauge length of 20 mm between the clamps (i.e., strain rate of 1.0 min^{-1}). The tests were conducted at room temperature. The tensile strength, Young's modulus, yield stress, and strain were all calculated from the force-elongation data recorded on the Instron chart. The following definitions were used in the calculations:

1. The engineering stress and strain were defined by

$$\sigma = \frac{F}{A_0}, \quad \epsilon = \frac{L - L_0}{L_0} = \frac{(\text{crosshead speed})(\text{chart distance})}{(\text{chart speed})(L_0)}$$

where F is the tensile force, L is the length of filament in the deformed state, and L_0 is the filament length in the initial state.

2. The Young's modulus, E , was defined as

$$E = \lim_{\epsilon \rightarrow 0} \frac{\Delta \sigma}{\Delta \epsilon}$$

where σ is the engineering stress, and ϵ is the engineering strain.

3. The tensile strength is the force at fracture divided by the original cross-sectional area, A_0 , of the filament.

Measurement of Poisson's Ratio

Poisson's ratio measurements were carried out using an Instron tensile tester. The procedure involved stretching the specimen between the Instron jaws at a strain rate of 1.0 min^{-1} and photographing the specimen at a predetermined strain of 0.02. This value of strain ensured that the deformations in all the samples were occurring in the elastic (linear) region. A reference sample of aluminum filament of diameter 3 mm was also mounted in between the Instron jaws and photographed. During the experiment, great caution was exercised to ensure that the mounted camera stayed at the same position. The final diameters were determined from the photographs. The Poisson's ratio was calculated from the definition:

$$\text{Poisson's ratio, } \nu = \frac{\text{Lateral strain}}{\text{Axial strain}}$$

Torsional Modulus Measurements

The torsional modulus measurements were carried out on the Mechanical Spectrometer. A special clamping device was constructed to firmly hold the samples and prevent any slippage. To eliminate the

effect of sample size in this type of measurement, filaments selected were about the same in diameter. To minimize buckling, 1 cm in length samples were used. To ensure that the same shear strain rate was imposed on the samples, it was necessary to set the spectrometer at the appropriate angular speed using the expression

$$\text{Shear rate} = \frac{\Omega r}{l}$$

where Ω is the angular speed, r is the radius, and l is the sample length. The value of this shear strain rate was the same as the strain rate used during tensile testing. It was also necessary to run the recording chart at a fast speed to capture the linear elastic deformation region. This was extremely important since the initial slope of the torque-angular displacement curve is needed in calculating the torsional modulus. The working equation is:

$$G = \frac{TL}{\phi J}$$

where G is the torsional modulus, T is the torque, L is the length of sample, ϕ is the angle turned through in radians, and J is the moment of inertia about the filament axis.

CHAPTER IV

BIREFRINGENCE, ORIENTATION, AND INTERNAL STRESSES IN THE FILAMENTS

A. RESULTS

Melt-Spinning

The filaments studied were prepared by melt-spinning through air. A molten threadline was stretched and cooled simultaneously between the spinneret and the take-up device. The tension measurements were carried out on-line while the birefringence measurements were carried out on the filaments collected at various take-up speeds at room temperature.

The birefringence of the spun filaments is negative, and its magnitude increases with take-up speed. Figure 4 shows the effect of spinning temperature on birefringence of PMMA filaments as a function of spinline stress. The plot indicates that there isn't any significant difference between the filaments melt-spun at 190°C and 200°C. The most striking feature about the plot is that the filaments melt-spun at 220°C show much higher rates of birefringence development with spinline stress and show a linear relationship between birefringence and spinline stress.

Temperature changes along the cooling threadline are an important variable in melt-spinning. This was investigated for melt-spinning of PMMA filaments at the spinning temperature of 190°C. Figure 5 illustrates the variation of temperature along the spinline for three different take-up speeds. The curves show there is rapid cooling taking place as soon as the filament leaves the spinneret and the filaments cool to room temperature at a short distance of about 21 cm below the spinneret.

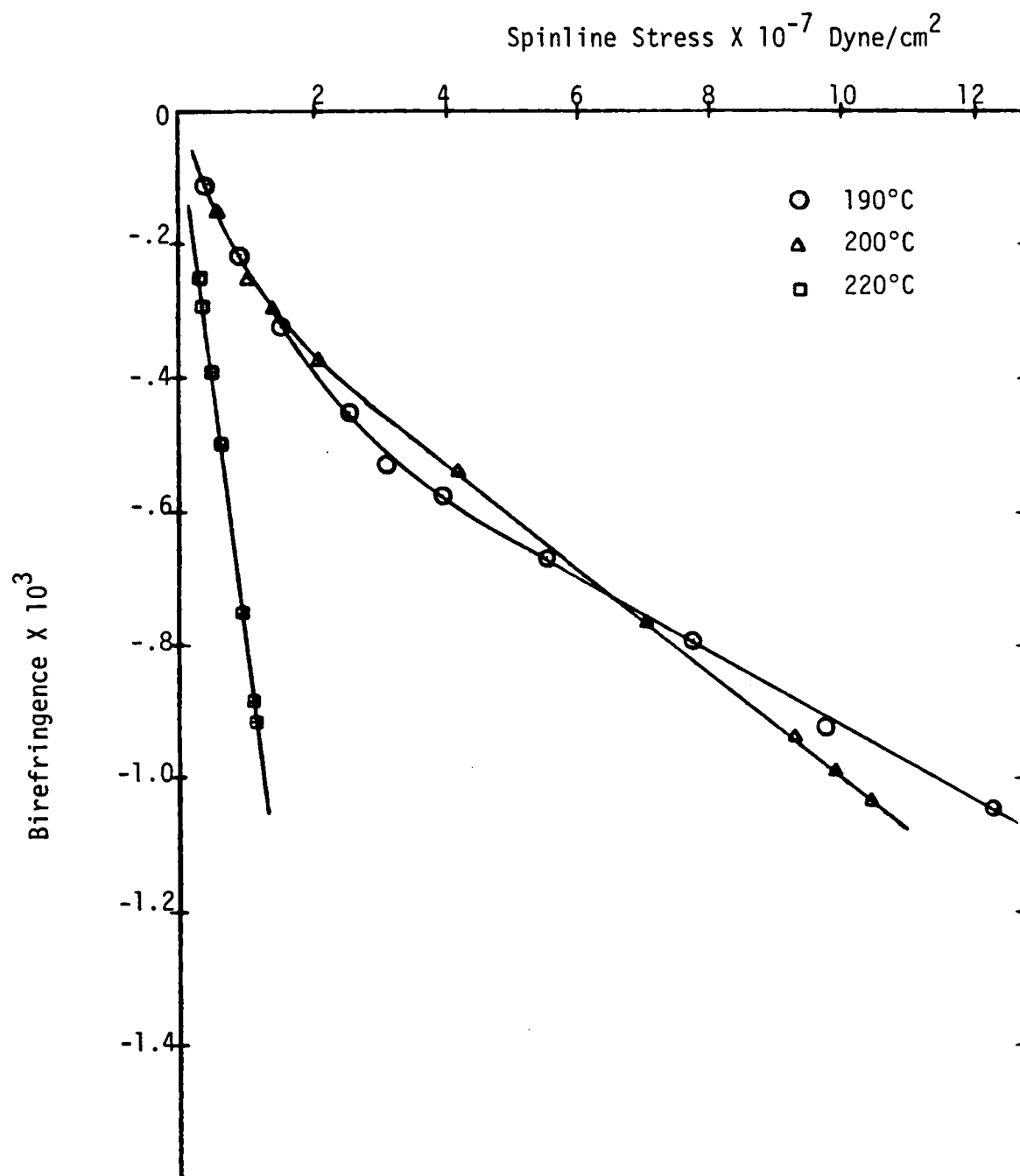


Figure 4: Effect of Spinning Temperature on Birefringence of PMMA Filaments as a Function of Spinline Stress.

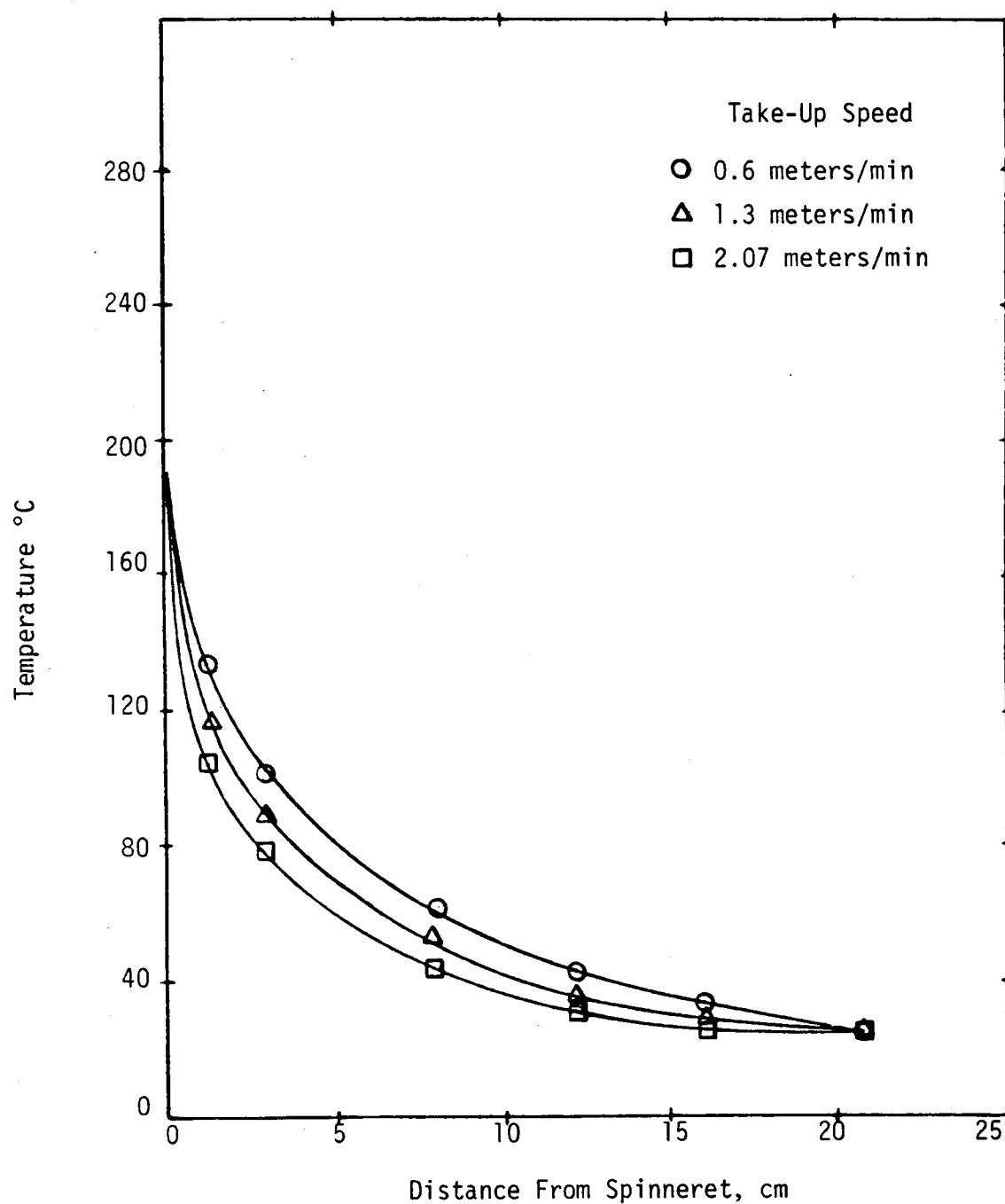


Figure 5: Temperature Variation Along the Spinline at Different Take-Up Speeds During Melt Spinning of PMMA at 190°C.

Temperature Dependence of Birefringence of Conditioned Melt-Spun Filaments

The results for temperature dependence of orientation birefringence for initially oriented PMMA filaments are shown in Figure 6. Temperatures higher than 80°C could not be reached because the filaments (restricted to constant length) broke just after reaching 80°C. Both curves show an appreciable change of orientation birefringence with temperature even though they are still in the glassy state. The curve for unrestricted filament shows a slightly faster decreasing rate in birefringence than that of the restricted filament. The results obtained for PS from the same experiment are shown in Figure 7. The curve for the unrestricted filament shows a constant decrease in birefringence with increasing temperature, while that of the restricted filament is essentially flat. This latter result has been reported in the literature (7).

Oven-Drawing of Filaments

The stress-birefringence relationship of both PMMA and PS were also investigated by the oven-drawing process. The birefringence of the filaments obtained from this process and the drawing temperature range of 107°C to 120°C was negative. The main difficulties encountered were efficient temperature control and breaking of filaments during drawing. More filaments broke at lower drawing temperatures than at higher drawing temperatures.

Typical force-elongation curves for PMMA and PS recorded on the Instron chart during the drawing process are shown in Figure 8. These curves suggest that there is a difference in behavior between PMMA and PS during the drawing process. They both show a drop in the load just before the cooling process, but unlike PS, which maintains almost a constant

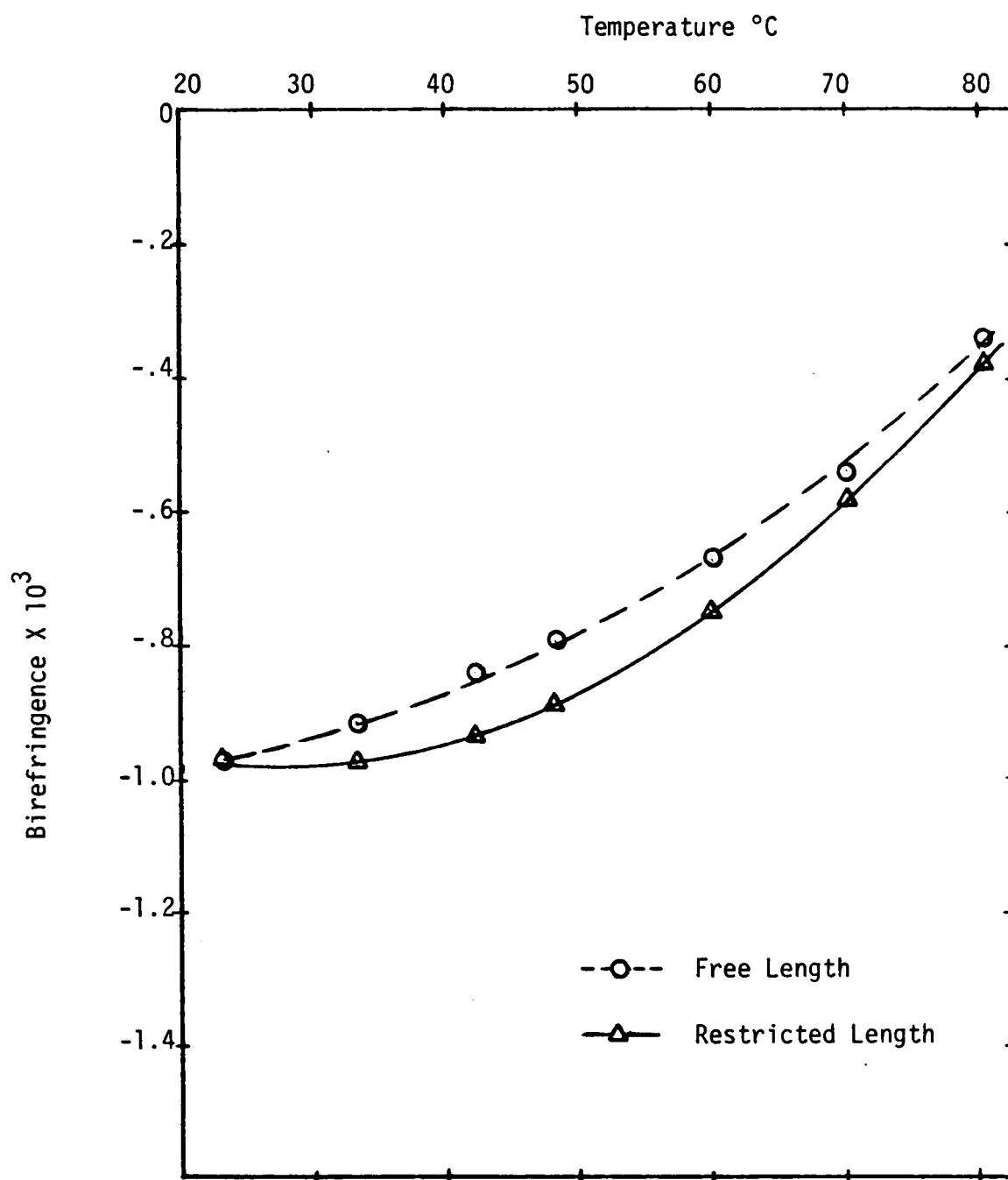


Figure 6: Temperature Dependence of Birefringence of Initially Oriented Filament of PMMA.

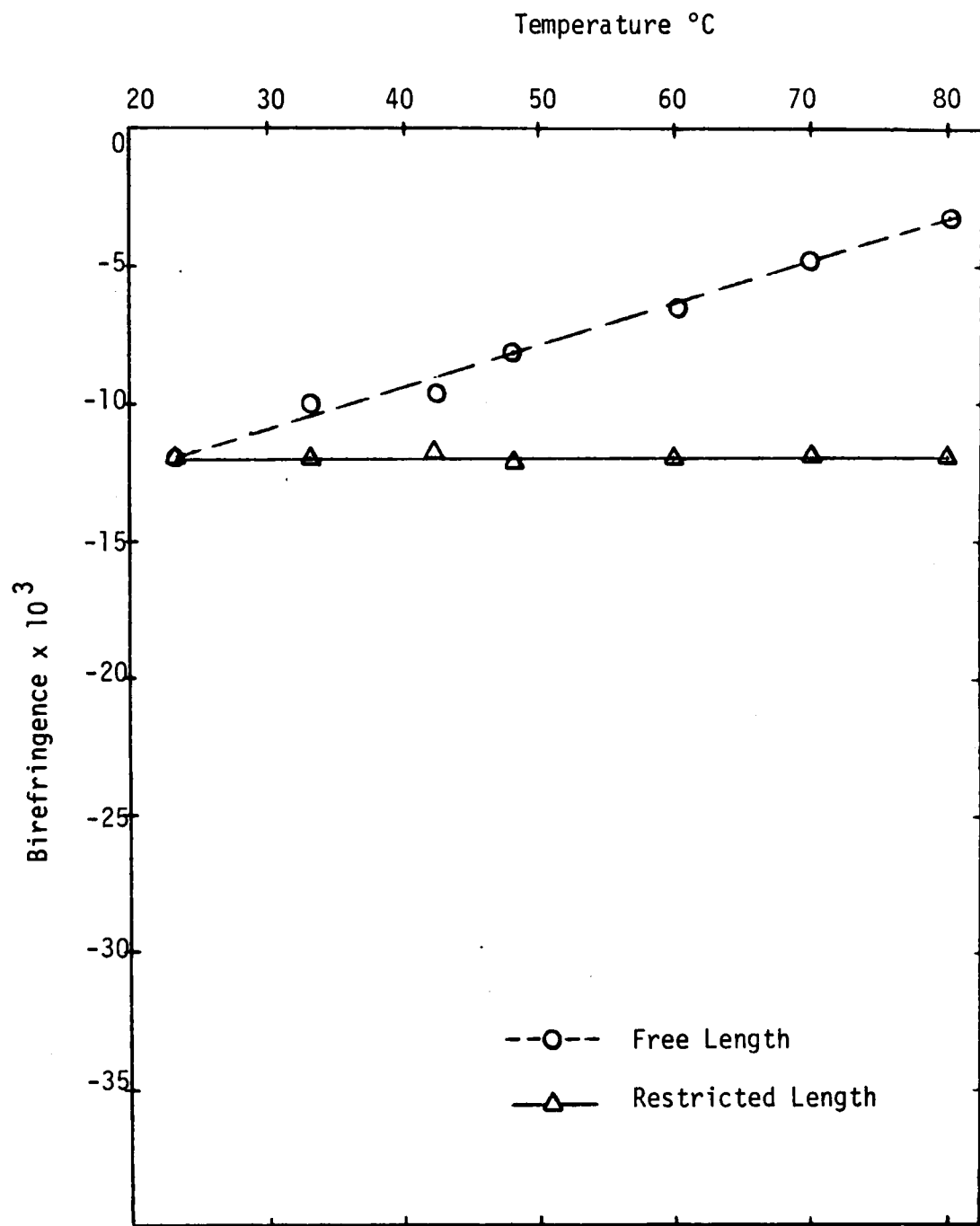


Figure 7: Temperature Dependence of Birefringence of Initially Oriented Filament of Polystyrene.

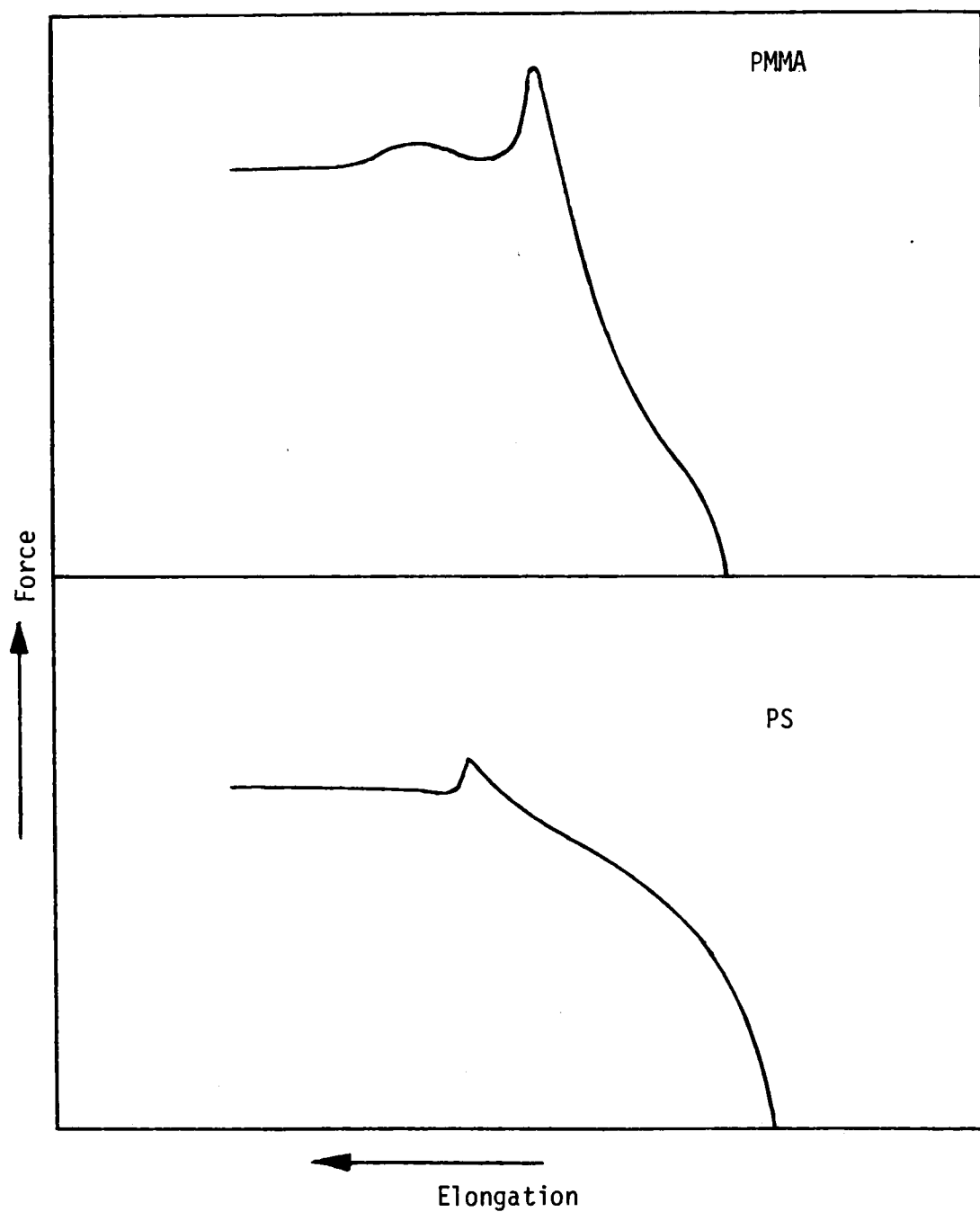


Figure 8: Typical Force-Elongation Curve for PMMA and PS Recorded on Instron Chart During Oven-Drawing Process.

force during cooling, PMMA shows a maximum before decreasing again to a constant load.

Figure 9 shows the effect of drawing temperature on birefringence of PMMA filaments as a function of vitrification stress. All the curves are non-linear and resemble those obtained for filaments melt-spun at 190°C and 200°C. Filaments drawn at 112°C show much higher birefringence development than the rest, especially at high stresses.

The result obtained for PS is illustrated in Figure 10. The plot shows that there is a linear relationship between birefringence and vitrification stress, and that this linear relationship is essentially independent of temperature within the range of temperatures used in this study (107°C-120°C). It can also be seen that the birefringence development is much higher than in the case of PMMA.

To investigate the effect of the levels of vitrification stress in this study, slopes of the curves (obtained for PMMA) calculated at constant stress levels were plotted against temperature. This is shown in Figure 11 with the data points connected by straight lines. It is evident that, in general, the slope increases in magnitude with decreasing stress at constant temperature. To effectively portray the relationship among the three variables--birefringence, vitrification stress, and temperature--it became necessary to generate a three-dimensional surface bounded by these variables. Figure 12 illustrates such a surface. Drawing at a temperature of 112°C clearly produces much higher birefringence than other temperatures, especially at high drawing stresses.

Figure 13 summarizes the effect of processing temperature on birefringence of PMMA filaments during melt-spinning and oven-drawing as a

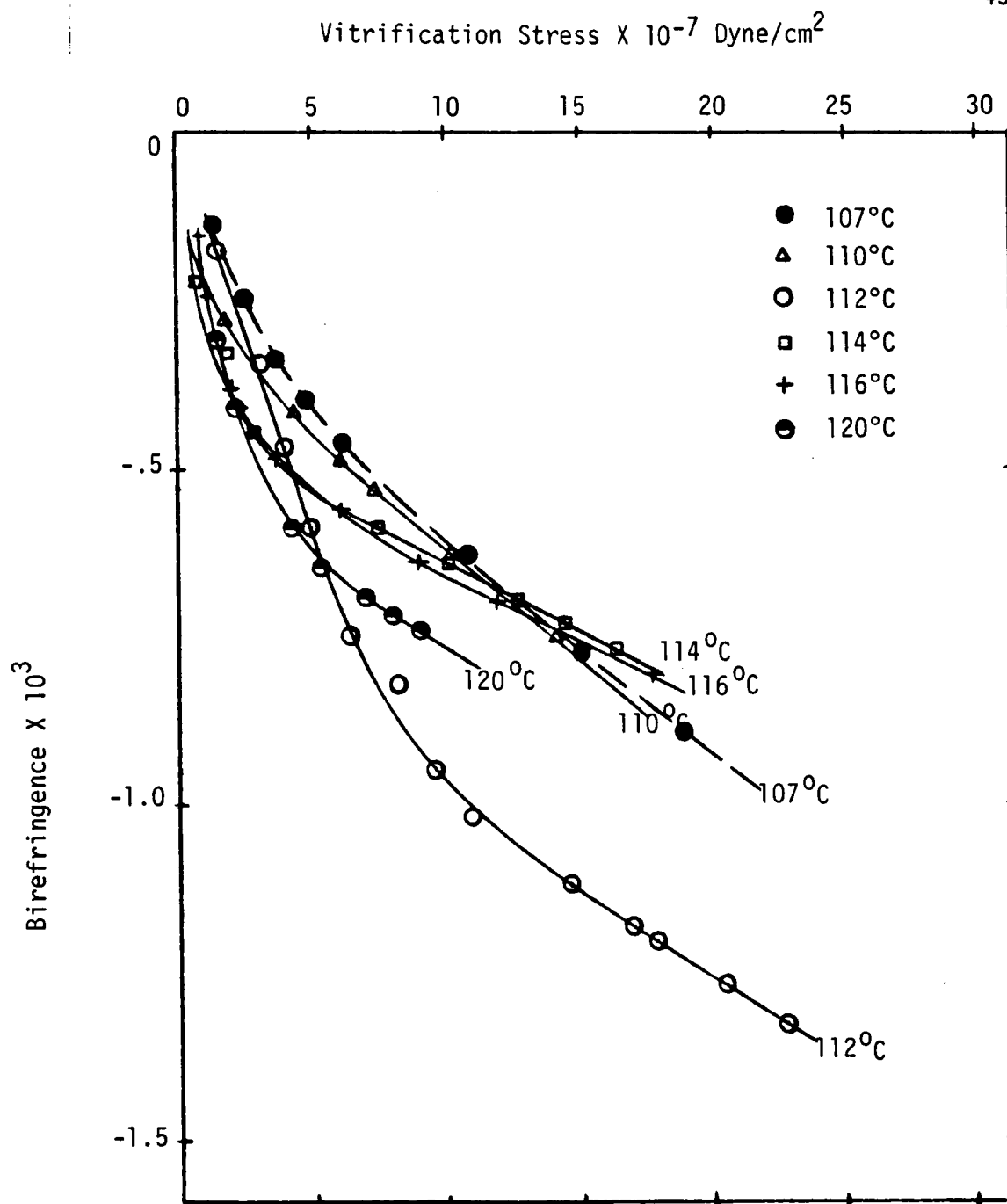


Figure 9: Effect of Drawing Temperature on Birefringence of PMMA Filaments as a Function of Vitrification Stress.

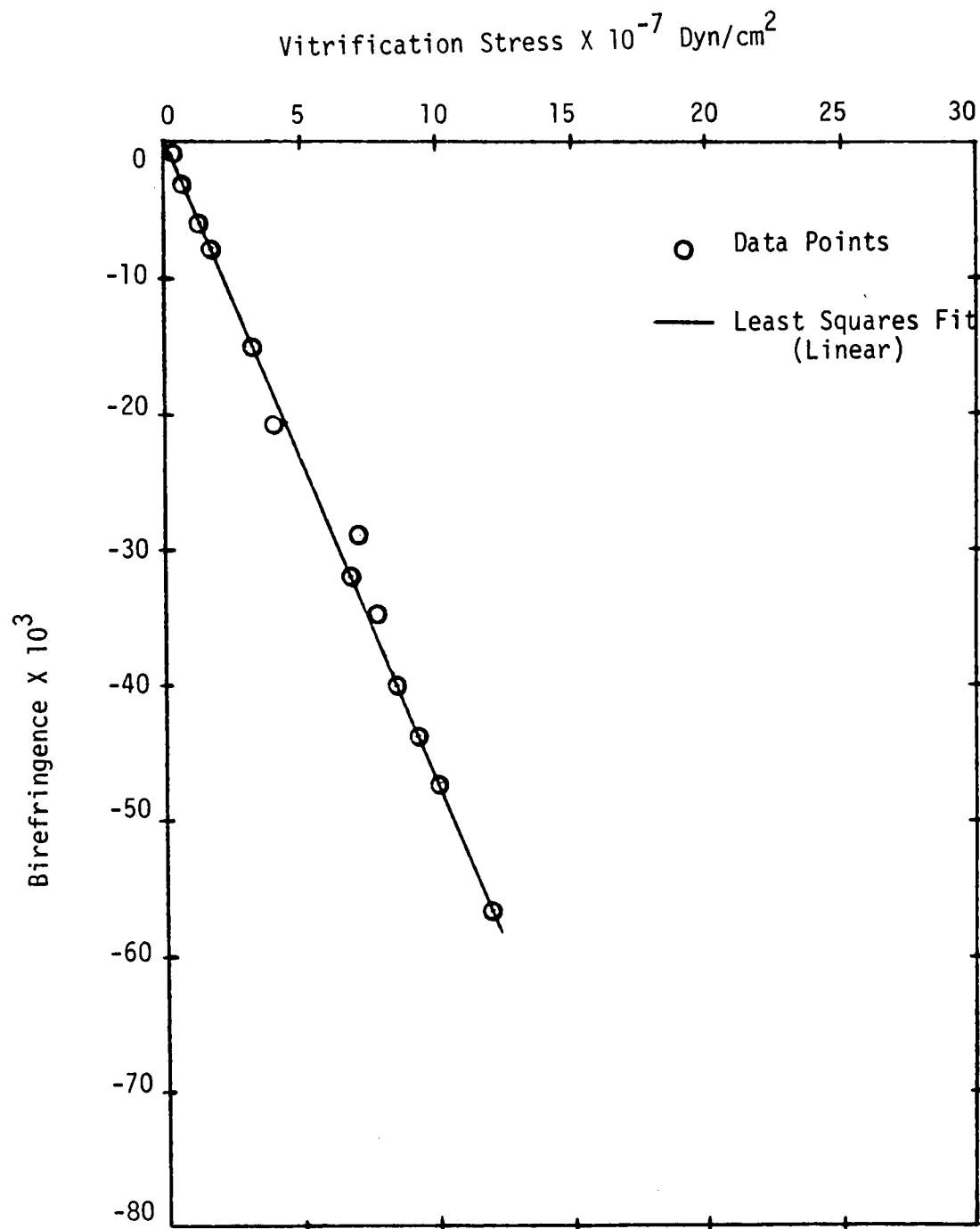


Figure 10: Variation of Birefringence of Oven-Drawn PS Filaments as a Function of Vitrification Stress. Drawing Temperatures 110°C-120°C.

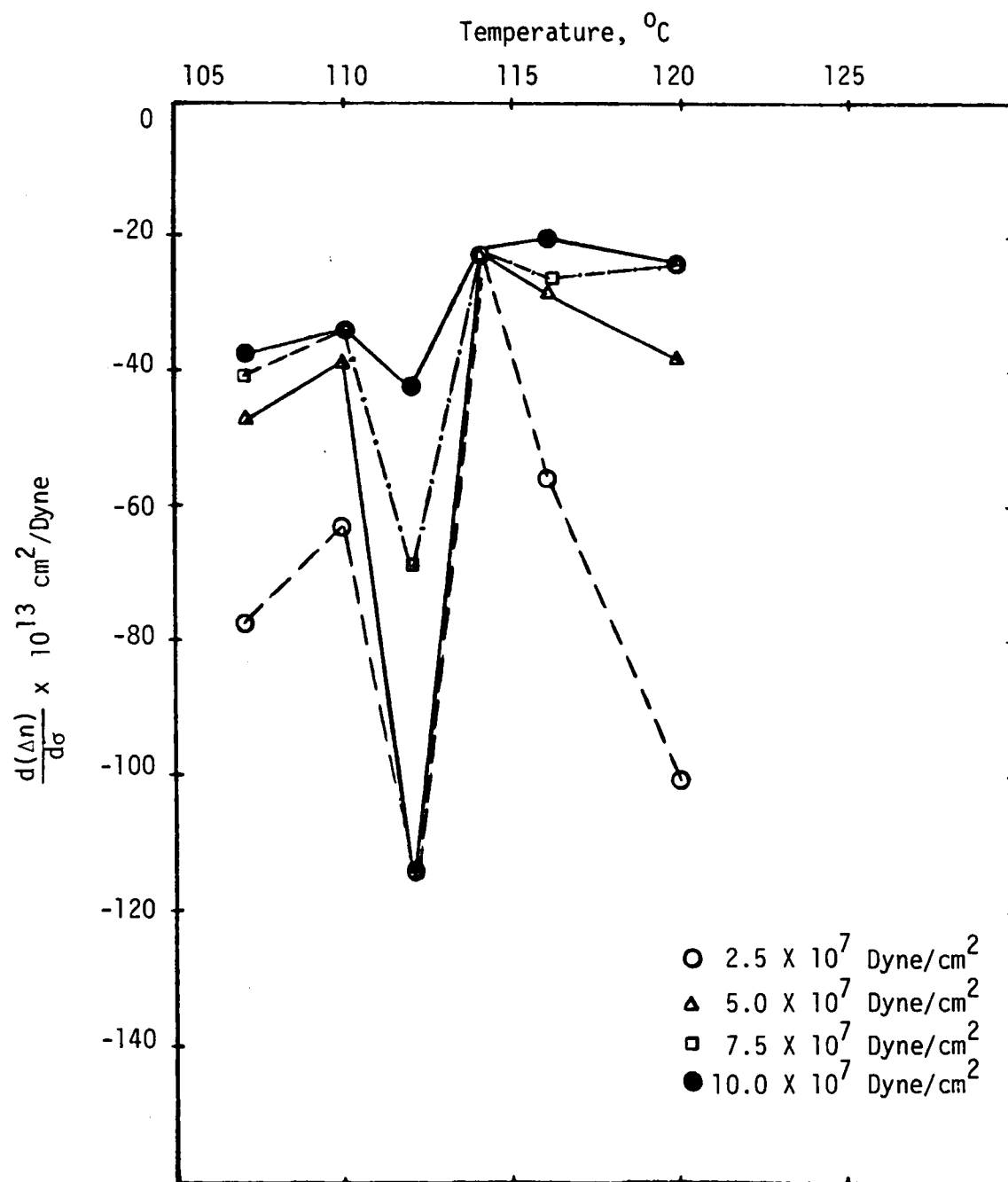


Figure 11: Effect of Stress on the Slope of Birefringence-Vitrification Stress as a Function of Drawing Temperature for Oven Drawn Filaments of PMMA.

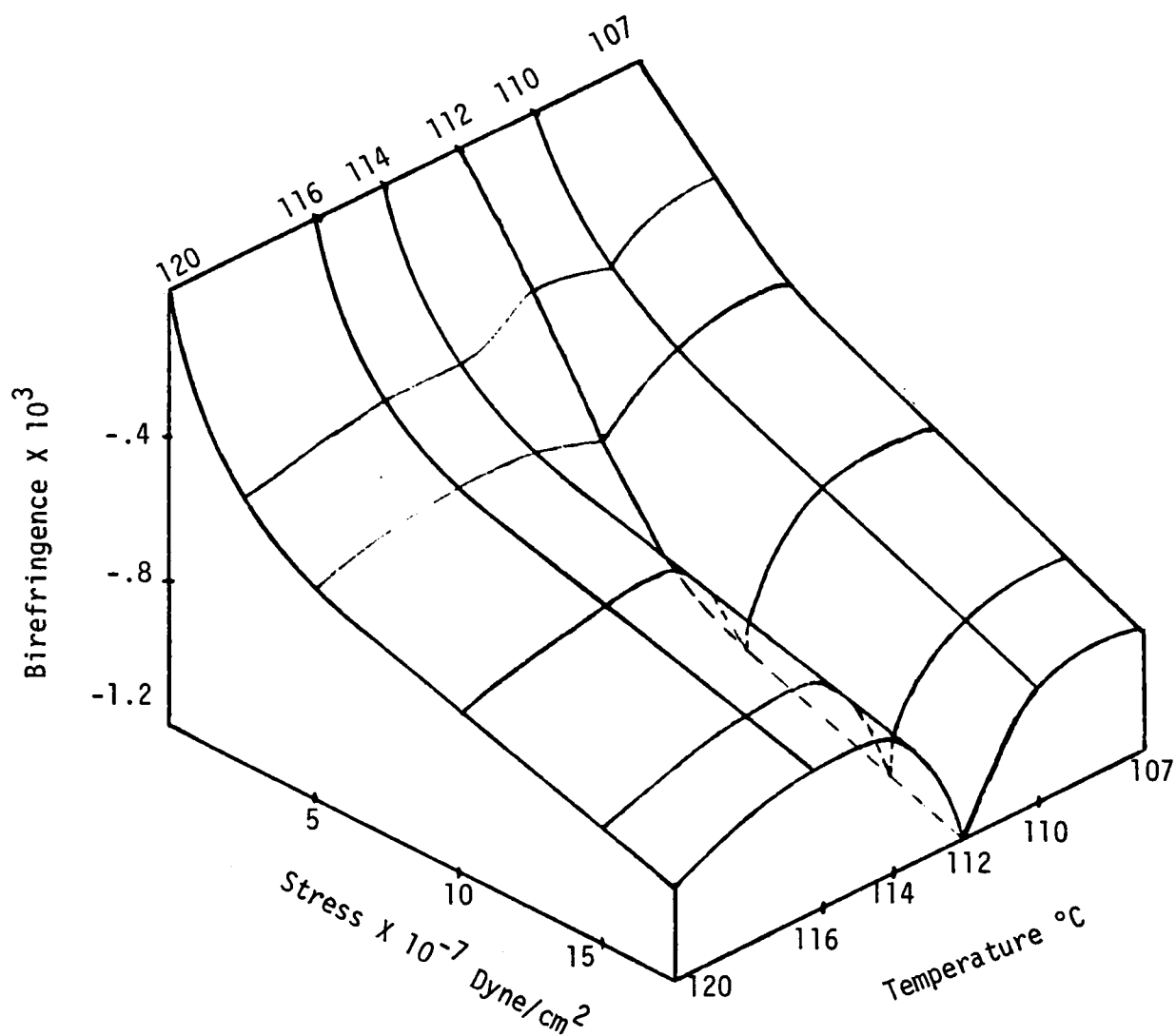


Figure 12: Three-Dimensional Surface Representation of Birefringence of Oven-Drawn PMMA Filaments as a Function of Vitrification Stress and Drawing Temperature.

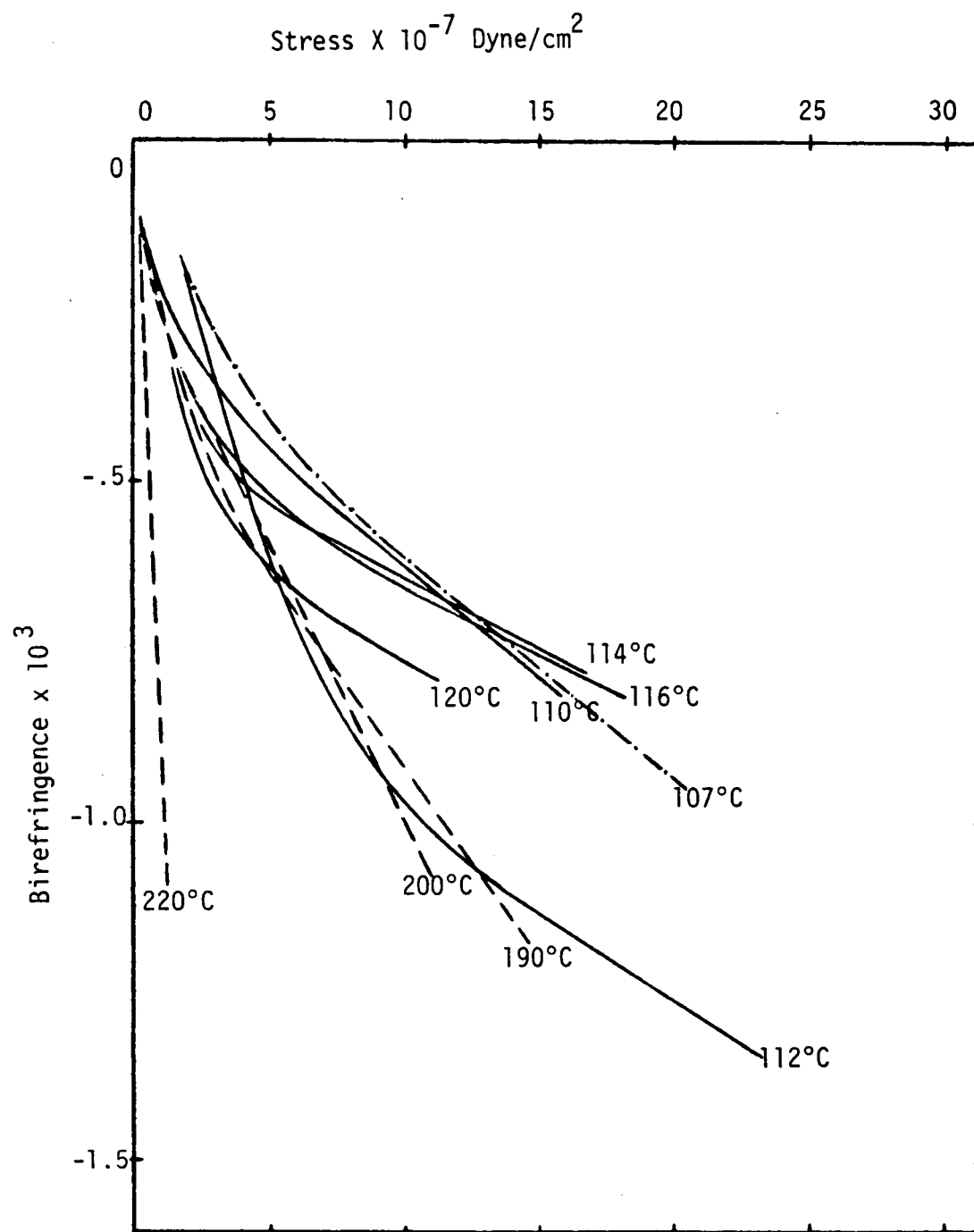


Figure 13: Effect of Processing Temperature on Birefringence of PMMA Filaments During Melt Spinning and Oven Drawing as a Function of Stress.

function of stress. It is interesting to note again that the filaments melt-spun at 220°C exhibit a marked difference in behavior from the rest. The filaments melt-spun at 190°C and 200°C have birefringence-stress behavior which falls within those of the oven-drawn filaments.

Birefringence Development for Extrusion into Air and Quench Baths

To investigate the possible effects of thermal stresses during melt-spinning, filaments of PMMA and PS were extruded into the air without take-up and allowed to cool. The birefringence of PMMA is negative, and that of PS is positive. The results are listed in Table II. The results indicate that for every extrusion temperature, birefringence decreases in magnitude with increasing filament diameter. Also, the higher the extrusion temperature, the greater the birefringence for filaments extruded through the same die.

In a parallel experiment, filaments were heated for about ten minutes in boiling water and were then quickly transferred into ice water bath containing some salt. The birefringence obtained for PMMA is negative, while that of PS is positive. These are shown in Table III and indicate that the birefringence developed due to rapid cooling decreases with increasing filament diameter. An interesting difference observed concerning these quenched filaments was that the PMMA filaments were found to be still transparent and very flexible, while those of PS were slightly milky in appearance and very brittle.

In another experiment, filaments of PMMA were extruded at temperatures from 170°C to 240°C into ice water bath. The results are shown in Figure 14. Again, it can be seen that the birefringence of the extruded filaments is negative and increases with increasing extrusion temperature.

TABLE II
BIREFRINGENCE OF AIR-QUENCHED FILAMENTS

180°C		200°C		220°C	
Diameter (cm)	Δn_3 ($\times 10^3$)	Diameter (cm)	Δn_3 ($\times 10^3$)	Diameter (cm)	Δn_3 ($\times 10^3$)
----- PMMA -----					
0.060	-0.06	0.056	-0.08	0.050	-0.09
0.129	-0.03	0.158	-0.05	0.134	-0.06
0.178	-0.02	0.160	-0.04	0.156	-0.05
----- PS -----					
0.059	+0.08	0.049	+0.09	0.035	+0.13
0.120	+0.05	0.092	+0.07	0.048	+0.11
0.140	+0.03	0.126	+0.05	0.058	+0.09

TABLE III
HEATING FOLLOWED BY RAPID QUENCHING IN
SALTED ICE WATER BATH

PMMA		PS	
Diameter (cm)	Δn ($\times 10^3$)	Diameter (cm)	Δn ($\times 10^3$)
0.093	-0.42	0.067	+0.55
0.095	-0.41	0.069	+0.54
0.115	-0.34	0.072	+0.51
0.116	-0.34	0.122	+0.48
0.124	-0.22	0.125	+0.42
0.207	-0.18		

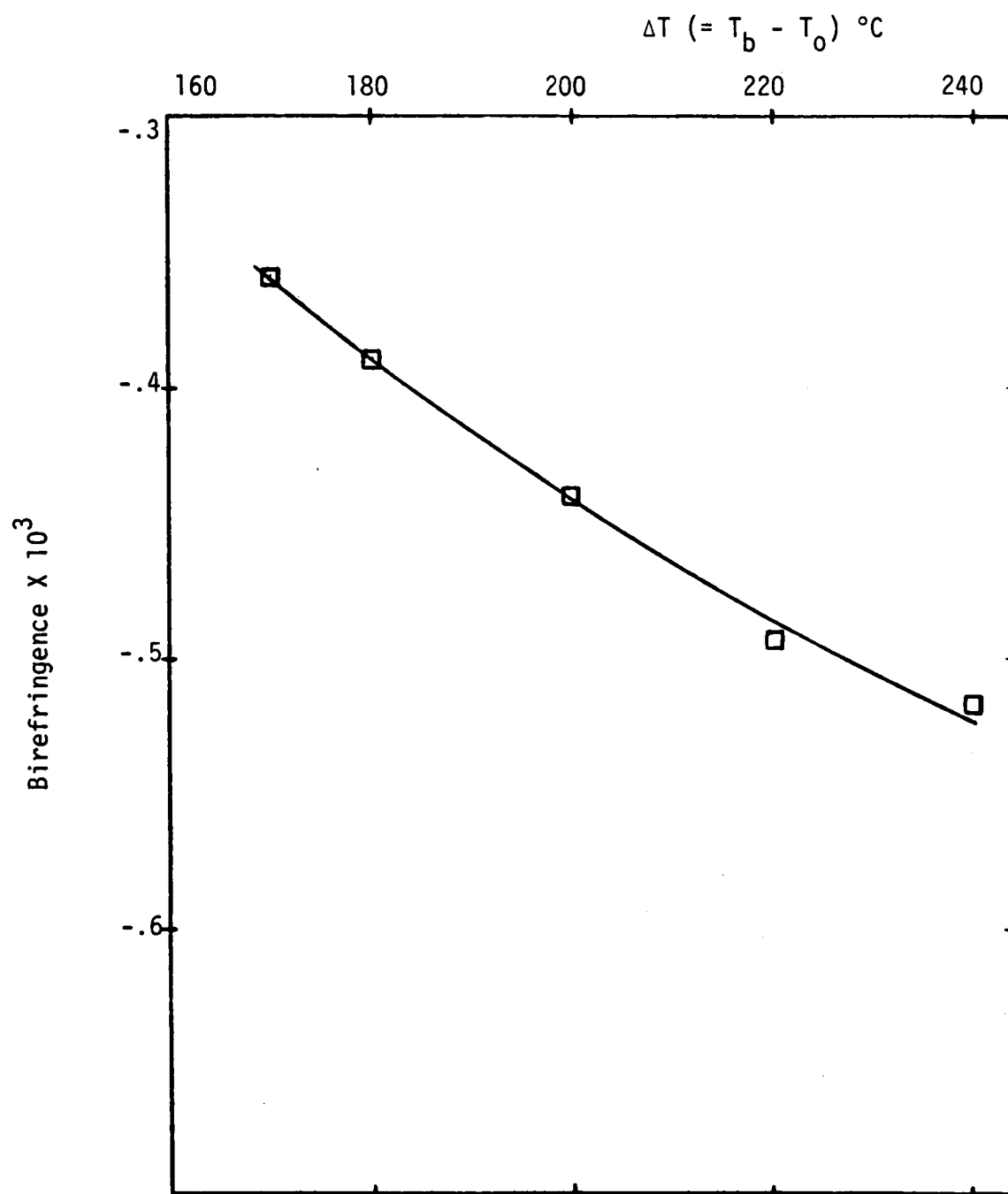


Figure 14: Effect of Spinning Temperature on Birefringence of PMMA Filaments Extruded Directly into Ice Water Bath.

B. INTERPRETATION

Birefringence and Orientation

Studies by Oda, White, and Clark (91) have shown that the frozen-in orientation distributions in polystyrene may be determined by application of rheo-optical laws relating stress and birefringence in the melt state and allowing the birefringence to be frozen near the glass transition temperature. (It has further been pointed out by various investigators that the birefringence does not completely represent the orientation but only yields a second moment of the distribution.) The negative birefringence exhibited by PS in this study can be explained by the above hypothesis. That is, the molecular orientation in the stressed polymer melt gives rise to birefringence, and this birefringence originated in the molten state where the stress-optical coefficient is negative is effectively frozen-in during vitrification.

In the case of melt-spun PMMA filaments, the negative birefringence values imply that even through the stress-optical coefficient of PMMA is positive at the spinning temperatures, the positive birefringence developed could not be frozen-in during vitrification. This is consistent with other studies (102,125) which have shown the positive birefringence developed in molten PMMA at elevated temperatures (temperatures greater than about 150°C) cannot be frozen-in during vitrification. On the other hand, negative birefringence is always obtained for oven-drawn PMMA filaments due to the negative stress-optical coefficient of PMMA at the drawing temperature range of 107°C to 120°C.

The negative birefringence exhibited by the melt-spun PMMA filaments is clearly inconsistent with the positive stress-optical coefficient

at the spinning temperatures of 190°C-220°C. However, if one accepts that $\Delta n = C(T)\sigma$ is obeyed above T_g , the birefringence could vary uniformly along the spinline until it reaches the neighborhood of T_g . Mechanistically, it has been suggested (7,125) that possibly the ester side group rotates during cooling such that at the transition region (about 150°C) the plane of the -COO- part which is a rigid planar structure is positioned in such a way that its effective polarizability is in a direction perpendicular to the main backbone plane. Then, consequently, there is the β relaxation (temperatures in the neighborhood of about 60°C) where independent or cooperative mechanisms of torsional oscillations around the main chain bond, and hindered rotations within the -COOCH₃ chain are possible.

As stated by Gurnee (43) and later investigators (134), the difference in polarization parallel and perpendicular to a polymer chain is dependent upon the averaged position of substituent groups relative to the chain axis, and if it varies with temperature, so would birefringence at constant orientation. This would explain the temperature dependence of birefringence in PMMA even in the solid state. That is, such changes in birefringence could be produced by the changes of molecular polarizability associated with the very small changes of intermolecular distance produced by thermal expansion or contraction. Another view (8) is that it is likely that there is a dipole-dipole association between the ester side groups in PMMA. This acts as effective crosslinks and dissociates progressively as temperature increases. PS, on the other hand, does not show any appreciable temperature dependence of birefringence. This has been attributed to the rigidity of the phenyl ring, which is unaffected

by temperature change, and also shows a lack of rotation about the connecting bond to the chain (6,7).

Thermal Stresses

Thermal stresses cannot be ignored in either of these experiments. Rapid and inhomogeneous cooling sets up temperature gradients in the filaments, with subsequent vitrification, resulting in thermal stress development. Stresses first build up as the filaments cool off and then relax as cooling proceeds further. The force-elongation plot recorded on the Instron chart during the oven-drawing process indicates (for PMMA) there appears to be an instant during the cooling period in which the stress passes through a maximum. This may be attributable to the fact that the thermal expansion coefficient in the rubbery region is greater than that of the glassy region. Thus, as the filament is cooling, it first contracts according to the higher expansion coefficient until the transition region, after which it contracts according to the smaller expansion coefficient. Clearly, one would expect quite substantial relaxation processes taking place in the neighborhood of T_g .

An important aspect of these thermal stresses resulting from rapid and inhomogeneous cooling and eventual vitrification is that they give rise to birefringence. The temperature profile and the associated stress profile at any instant during cooling of the filament can be calculated. The calculation is based on the theoretical analysis, the detailed formulation of which is presented in Appendix B. The two different hypotheses upon which the calculations are based are as follows:

1. The stress distribution at time t_{gc} (the time when the center temperature has reached T_g) is effectively frozen-in.
2. The stress distribution at time t_{g1} (the time when an outer shell of thickness $0.1a$ has solidified such that the temperature at $r = 0.9a$ is T_g) is effectively frozen-in.

The temperature distributions corresponding to t_{gc} and t_{g1} are given as (see Appendix B):

$$T(r, t_{gc}) - T_s = (T_g - T_s) J_0(\beta_1 \frac{r}{a}) \quad (IV-1a)$$

$$T(r, t_{g1}) - T_s = (T_g - T_s) \frac{J_0(\beta_1 \frac{r}{a})}{J_0(0.9\beta_1)} \quad (IV-1b)$$

These temperature profiles are shown in Figure 15 for both PMMA and PS.

The stress distributions are given by

$$\frac{(1 - \nu)\sigma_{rr}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [J_1(\beta_1) - \frac{a}{r} J_1(\beta_1 \frac{r}{a})] A \exp \frac{-\kappa\beta_1^2}{a^2} t \quad (IV-2a)$$

$$\frac{(1 - \nu)\sigma_{\theta\theta}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [J_1(\beta_1) + \frac{a}{r} J_1(\beta_1 \frac{r}{a}) - \beta_1 J_0(\beta_1 \frac{r}{a})] A \exp \frac{-\kappa\beta_1^2}{a^2} t \quad (IV-2b)$$

$$\frac{(1 - \nu)\sigma_{zz}}{E(T_0 - T_s)} = \frac{1}{\beta_1} [2\nu J_1(\beta_1) - \beta_1 J_0(\beta_1 \frac{r}{a})] A \exp \frac{-\kappa\beta_1^2}{a^2} t \quad (IV-2c)$$

The stress profiles corresponding to the above expressions are shown in Figures 16-17 for PMMA and PS. They are obtained by substituting t_{gc} and t_{g1} in place of t in the stress expressions. The plots show that the

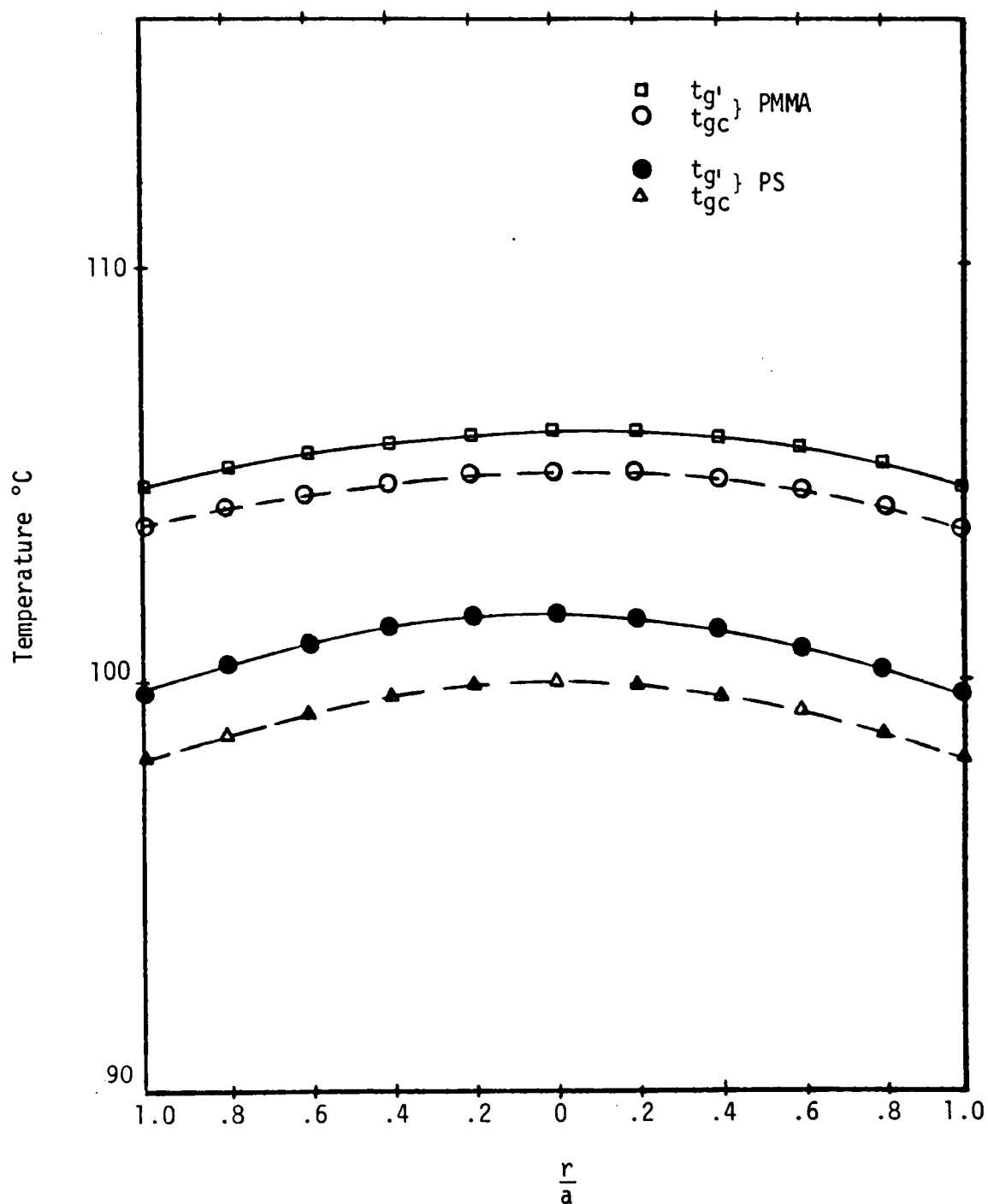


Figure 15: The Temperature Profiles Corresponding to t_{gc} and t_g' For Both PMMA and PS.

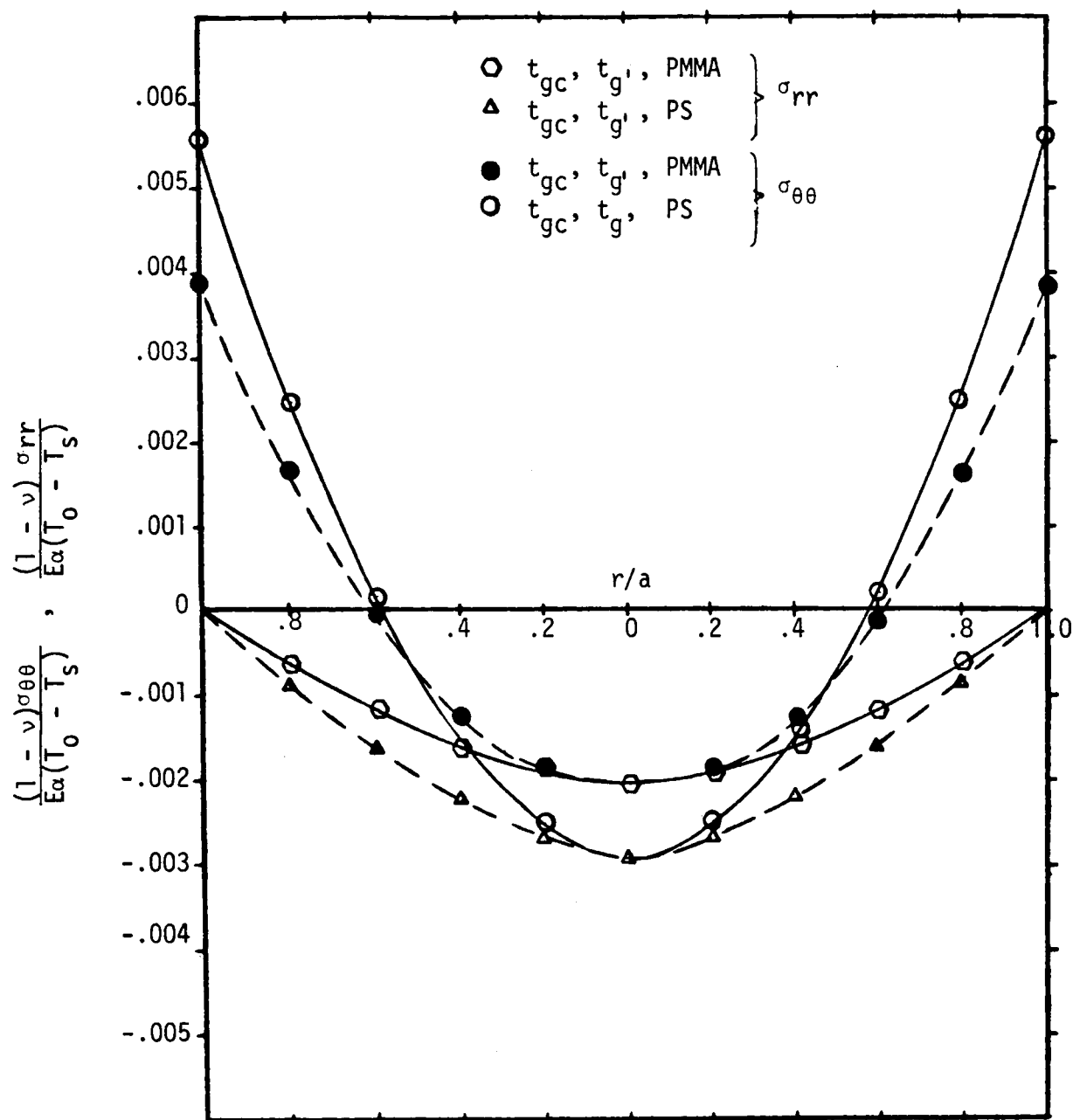


Figure 16: The Dimensionless Radial and Tangential Stress Profiles Corresponding to t_{gc} and $t_{g'}$ for Both PMMA and PS.

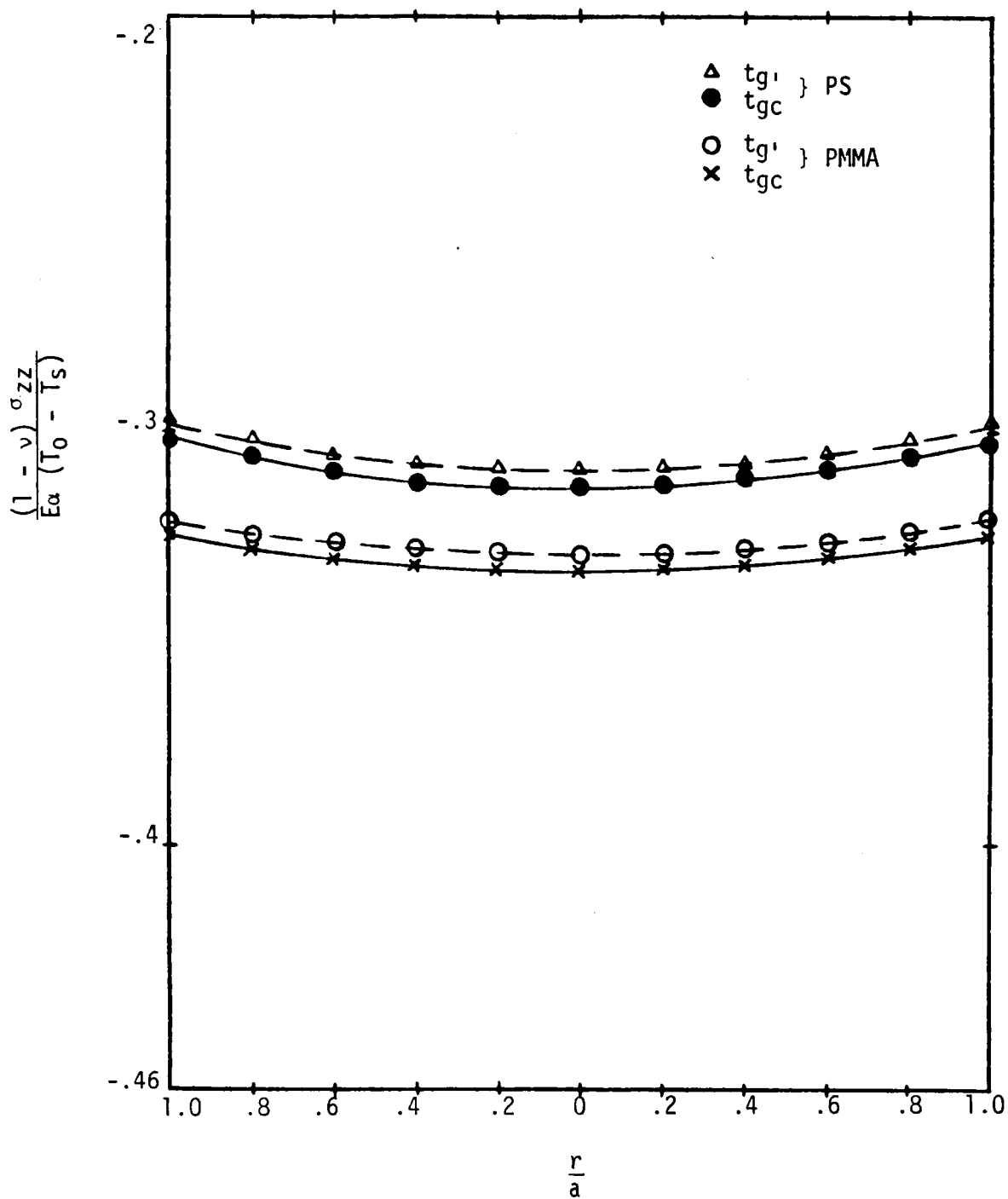


Figure 17: The Dimensionless Axial Stress Profiles Corresponding to t_{gc} and $t_{g'}$ for Both PMMA and PS.

radial and tangential stress profiles corresponding to t_{gc} and t_g , are identical, and that it is only in the axial stress that there is a slight difference. The detailed calculations for t_{gc} , t_g , and average stresses are shown below.

PMMA

$$a = 0.02 \text{ cm}; \quad V_z = 2.03 \frac{\text{cm}}{\text{sec}}; \quad \rho = 1.19 \frac{\text{g}}{\text{cm}^3}; \quad W = 0.00303 \frac{\text{g}}{\text{sec}}$$

from

$$h = 0.21(1 + M)k_0 \sqrt{\frac{\pi \rho V_z}{W}} \left(\frac{2}{v_0}\right)^{0.334} \left(\frac{\rho W V_z}{\pi}\right)^{0.117}$$

where

$$k_0 = 5.97 \times 10^{-5} \text{ cal/cm} \cdot \text{s} \cdot ^\circ\text{C}$$

$$v_0 = 14.2 \times 10^{-2} \text{ cm}^2/\text{s}.$$

(See Appendix B for the definition of these terms.) If M is taken to be 0, then

$$h = 7.47 \times 10^{-4} \text{ cal/cm}^2 \cdot \text{s} \cdot ^\circ\text{C}; \quad \frac{ah}{k} = 0.03$$

where

$$k = 5 \times 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot ^\circ\text{C}.$$

Using Equation (B-4),

$$\beta_1 = 0.244; \quad \kappa = 12.004 \times 10^{-4} \text{ cm}^2/\text{s}; \quad C = 0.35 \text{ cal/g} \cdot ^\circ\text{C}.$$

From

$$\frac{T(r, t) - T_s}{T_o - T_s} = A \exp \frac{-\kappa \beta_1^2}{a^2} t J_o \left(\beta_1 \frac{r}{a} \right)$$

where

$$A = 1.0045,$$

t_{gc} is given by

$$\frac{T_g - T_s}{T_o - T_s} = (1.0045)(e^{-0.1785 t_{gc}})(1)$$

$$t_{gc} = 4.006 \text{ sec};$$

$t_{g'}$ is given by

$$\frac{T_g - T_s}{T_o - T_s} = (1.0045)(e^{-0.1785 t_{g'}})[J_o(0.9 \times 0.244)]$$

$$t_{g'} = 3.936 \text{ sec.}$$

The corresponding average stresses are given by (See Equations [B-12a] through [B-12C] in Appendix B.):

For t_{gc} ,

$$\frac{(1 - \nu)\sigma_{rr_{av}}}{E\alpha(T_o - T_s)} = 2.01197[2J_1(0.244) - \int_0^{0.244} J_o(x)dx] = -0.001448;$$

for $t_{g'}$,

$$\frac{(1 - \nu)\sigma_{rr_{av}}}{E\alpha(T_0 - T_s)} = 2.03757[2J_1(0.244) - \int_0^{0.244} J_0(x)dx] = -0.001467;$$

for t_{gc} and $t_{g'}$,

$$\frac{(1 - \nu)\sigma_{\theta\theta_{av}}}{E\alpha(T_0 - T_s)} = 0;$$

for t_{gc} ,

$$\frac{(1 - \nu)\sigma_{zz_{av}}}{E\alpha(T_0 - T_s)} = 2.01197[0.66J_1(0.244) - \int_0^{0.244} J_0(x)dx] = -0.327615;$$

for $t_{g'}$,

$$\frac{(1 - \nu)\sigma_{zz_{av}}}{E\alpha(T_0 - T_s)} = 2.03757[0.66J_1(0.244) - \int_0^{0.244} J_0(x)dx] = -0.331784;$$

where

$$\int_0^{0.244} J_0(x)dx = 0.24268, \text{ from trapezoidal rule.}$$

Using

$$\nu = 0.33; \quad E = 2.8 \times 10^{10} \text{ dyne/cm}^2; \quad \alpha = 0.8 \times 10^{-4} \text{ } ^\circ\text{C}^{-1};$$

$$T_0 = 190^\circ\text{C}; \quad T_s = 23^\circ\text{C},$$

for t_{gc} ,

$$\sigma_{rr_{av}} = -0.808 \times 10^6 \text{ dyne/cm}^2; \quad \sigma_{zz_{av}} = -182.9 \times 10^6 \text{ dyne/cm}^2;$$

for $t_{g'}$,

$$\sigma_{rr_{av}} = -0.819 \times 10^6 \text{ dyne/cm}^2; \quad \sigma_{zz_{av}} = -185.2 \times 10^6 \text{ dyne/cm}^2.$$

The birefringence associated with the stresses is given by (from stress-optical law):

$$\Delta n = C(\sigma_{zz_{av}} - \sigma_{rr_{av}})$$

where C is the room temperature stress-optical coefficient.

For t_{gc} ,

$$\Delta n = (-4 \times 10^{-13} \frac{\text{cm}^2}{\text{dyne}})(182.9 - 0.808) \times 10^6 \frac{\text{dyne}}{\text{cm}^2} = -0.073 \times 10^{-3}.$$

For $t_{g'}$,

$$\Delta n = (-4 \times 10^{-13} \frac{\text{cm}^2}{\text{dyne}})(185.2 - 0.819) \times 10^6 \frac{\text{dyne}}{\text{cm}^2} = -0.074 \times 10^{-3}.$$

PS

$$a = 0.02 \text{ cm}; \quad V_z = 2.03 \text{ cm/sec}; \quad \rho = 1.07 \text{ g/cm}^3; \quad W = 0.00303 \text{ g/sec};$$

$$h = 7.0 \times 10^{-4} \text{ cal/cm}^2 - \text{s} - ^\circ\text{C}.$$

$$\frac{ah}{k} = 0.049$$

where

$$k = 2.85 \times 10^{-4} \text{ cal/cm} - \text{s} - ^\circ\text{C}.$$

$$\beta_1 = 0.311; \quad \kappa = 8.32 \times 10^{-4} \text{ cm}^2/\text{s}; \quad C = 0.32 \text{ cal/g} - ^\circ\text{C}.$$

From

$$\frac{T(r, t) - T_s}{T_0 - T_s} = A \exp \frac{-\kappa \beta_1^2}{a^2} t J_0 \left(\beta_1 \frac{r}{a} \right)$$

where

$$A = 1.0157,$$

 t_{gc} is given by

$$\frac{T_g - T_s}{T_0 - T_s} = (1.0157)(e^{-0.2012 t_{cg}})(1)$$

$$t_{gc} = 3.926 \text{ sec};$$

 t_g is given by

$$\frac{T_g - T_s}{T_o - T_s} = (1.0157)(e^{-0.2012 t_{g'}})[J_o(0.9 \times 0.311)]$$

$$t_{g'} = 3.826 \text{ sec.}$$

The corresponding average stresses are given by:

For t_{gc} ,

$$\frac{(1 - \nu)\sigma_{rr_{av}}}{E\alpha(T_o - T_s)} = 1.4823[2J_1(0.311) - \int_0^{0.311} J_o(x)dx] = -0.001867;$$

for $t_{g'}$,

$$\frac{(1 - \nu)\sigma_{rr_{av}}}{E\alpha(T_o - T_s)} = 1.4976[2J_1(0.311) - \int_0^{0.311} J_o(x)dx] = -0.001887;$$

for t_{gc} and $t_{g'}$,

$$\frac{(1 - \nu)\sigma_{\theta\theta_{av}}}{E\alpha(T_o - T_s)} = 0;$$

for t_{gc} ,

$$\frac{(1 - \nu)\sigma_{zz_{av}}}{E\alpha(T_o - T_s)} = 1.4823[0.66J_1(0.311) - \int_0^{0.311} J_o(x)dx] = -0.306881;$$

for $t_{g'}$,

$$\frac{(1 - \nu)\sigma_{zz_{av}}}{E\alpha(T_0 - T_s)} = 1.4976[0.66J_1(0.311) - \int_0^{0.311} J_0(x)dx] = -0.310048;$$

where

$$\int_0^{0.311} J_0(x)dx = 0.30838, \text{ from trapezoidal rule.}$$

Using

$$\begin{aligned} \nu &= 0.33; & E &= 3.4 \times 10^{10} \text{ dyne/cm}^2; & \alpha &= 0.7 \times 10^{-4} \text{ }^\circ\text{C}^{-1}; \\ T_0 &= 190^\circ\text{C}; & T_s &= 23^\circ\text{C}, \end{aligned}$$

for t_{gc} ,

$$\sigma_{rr_{av}} = -1.1075 \times 10^6 \text{ dyne/cm}^2; \quad \sigma_{zz_{av}} = -182.05 \times 10^6 \text{ dyne/cm}^2;$$

for $t_{g'}$,

$$\sigma_{rr_{av}} = -1.1194 \times 10^6 \text{ dyne/cm}^2; \quad \sigma_{zz_{av}} = -183.93 \times 10^6 \text{ dyne/cm}^2.$$

The birefringence associated with the stresses is given by:

$$\Delta n = C(\sigma_{zz_{av}} - \sigma_{rr_{av}}).$$

For t_{gc} ,

$$\Delta n = (10 \times 10^{-13} \frac{\text{cm}^2}{\text{dyne}})(182.05 - 1.1075) \times 10^6 \frac{\text{dyne}}{\text{cm}^2} = 0.181 \times 10^{-3}.$$

For $t_{g'}$,

$$\Delta n = (10 \times 10^{-13} \frac{\text{cm}^2}{\text{dyne}})(183.93 - 1.1194) \times 10^6 \frac{\text{dyne}}{\text{cm}^2} = 0.183 \times 10^{-3}.$$

The results of average stress and birefringence calculated based on the two hypotheses are summarized in Table IV.

From Table IV, it can be seen that both hypotheses yield nearly identical results. The birefringence values are of the same order of magnitude as those obtained for filaments which were extruded into air directly without any take-up. This seems to suggest that the thermal stress analysis used in this study is at least valid. It can also be inferred from the results that the stress distribution in the filament just after the surface temperature has reached T_g is effectively frozen-in during subsequent cooling to room temperature.

The temperature profiles corresponding to $t_{g'}$ and t_{gc} indicate a very high cooling rate of about $14^\circ\text{C}/\text{sec}$ and $16^\circ\text{C}/\text{sec}$ for PMMA and PS respectively, and this results in extremely high stress levels. It must be pointed out that the analysis only gives a rough estimate of the residual thermal stresses since it does not take into account the following:

1. Viscoelasticity and temperature dependence of the mechanical properties. The viscoelasticity above and around T_g can be conveniently ignored provided

TABLE IV
SUMMARY OF CALCULATED AVERAGE STRESS AND BIREFRINGENCE

Average Stress	PMMA			PS		
	$\sigma_{rr\text{ av}}$ ($\times 10^{-6} \frac{\text{dyne}}{\text{cm}^2}$)	$\sigma_{zz\text{ av}}$ ($\times 10^{-6} \frac{\text{dyne}}{\text{cm}^2}$)	Δn_3 ($\times 10^{-3}$)	$\sigma_{rr\text{ av}}$ ($\times 10^{-6} \frac{\text{dyne}}{\text{cm}^2}$)	$\sigma_{zz\text{ av}}$ ($\times 10^{-6} \frac{\text{dyne}}{\text{cm}^2}$)	Δn_3 ($\times 10^{-3}$)
Based on t_{gc}	-0.808	-182.9	-0.073	-1.108	-182.05	0.181
Based on t_g'	-0.819	-185.9	-0.074	-1.119	-183.93	0.183

that the initial melt temperature is not too close to T_g . However, in the glassy state, the viscoelastic effects and temperature dependences cannot be ignored, and neither can the volume-relaxation effects and temperature dependence of the expansivity. Effective analysis should incorporate expansivity and modulus as functions of the momentary and local value of temperature.

2. Mechanical non-linearities and yielding due to very high stresses cannot be ignored. This is essential because stresses may become so large that they exceed the limits of linear viscoelastic behavior.

Implications

Clearly, it is evident that the birefringence exhibited by the oven-drawn and melt-spun filaments in these experiments is made up of contributions from both residual thermal stresses and flow-induced orientation. Specifically, the birefringence arising from rapid and inhomogeneous cooling and eventual vitrification is superimposed on the birefringence due to molecular orientation. Thus, if one assumes that the stress-optical law holds in both cases, then for birefringence due to flow-induced orientation,

$$\Delta n = C(T_g)\sigma_{\text{vitrification}}$$

where $\sigma_{\text{vitrification}}$ = drawing stress for the case of oven-drawing, or spinline stress for the case of melt-spinning. For birefringence due to thermal stress,

$$\Delta n = C(T_{\text{room}})\sigma_{\text{thermal}}.$$

The total birefringence in the filament may theoretically be given as

$$\Delta n_{\text{total}} = C(T_{\text{room}})\sigma_{\text{thermal}} + C(T_g)\sigma_{\text{vitrification}}.$$

This expression is only approximately true, and it does not account for the possible interaction between the two phenomena. However, for comparative purposes, a typical model calculation based on the above expression can be carried out for both PMMA and PS using thermal stress values corresponding to identical Fourier numbers in each case. The calculation is as follows:

Assuming in each case that

$$\sigma_{\text{vitrification}} = 5.0 \times 10^7 \text{ dyne/cm}^2,$$

for PMMA,

$$C(T_{\text{room}})\sigma_{\text{thermal}} = -0.073 \times 10^{-3} \quad (\text{from Table IV})$$

$$\begin{aligned} C(T_g)\sigma_{\text{vitrification}} &= (-41 \times 10^{-13} \frac{\text{cm}^2}{\text{dyne}})(5 \times 10^7 \frac{\text{dyne}}{\text{cm}^2}) \\ &= -0.21 \times 10^{-3} \end{aligned}$$

$$\Delta n_{\text{total}} = -0.28 \times 10^{-3}.$$

Similarly, for PS,

$$C(T_{\text{room}})\sigma_{\text{thermal}} = 0.181 \times 10^{-3} \quad (\text{from Table IV})$$

$$\begin{aligned} C(T_g)\sigma_{\text{vitrification}} &= (-4700 \times 10^{-13} \frac{\text{cm}^2}{\text{dyne}})(5 \times 10^7 \frac{\text{dyne}}{\text{cm}^2}) \\ &= -23.5 \times 10^{-3} \end{aligned}$$

$$\Delta n_{\text{total}} = -23.32 \times 10^{-3}.$$

It is evident from these calculations that the birefringence in the filaments is mostly due to molecular orientation; the thermal stress contribution is about 26% in PMMA and only about 0.78% in PS. Thus, the birefringence due to thermal stress has much greater relative contribution to the total birefringence in PMMA than in PS. The thermal stress effect is greatest at low drawing or spinning stresses and diminishes as the drawing or spinning stress increases. This could explain the non-linear birefringence-stress behavior of PMMA.

CHAPTER V

MECHANICAL PROPERTIES

A. RESULTS

The oriented PMMA filaments studied in this research were prepared in two different ways: by melt-spinning and by oven-drawing. The mechanical properties of these oriented filaments will be treated as a function of birefringence. The birefringence of both melt-spun and oven-drawn filaments is negative. The tensile measurements were obtained on an Instron machine using a specimen length of 2.0 cm between the clamps and an initial strain rate of 1.0 min^{-1} .

Deformation Oriented Filaments

Filaments melt-spun at 180°C had birefringence ranges of -0.34×10^{-3} to -1.00×10^{-3} and diameter ranges of 0.032 to 0.082 cm. Filaments melt-spun at 200°C had birefringence ranges of -0.22×10^{-3} to -1.05×10^{-3} and diameter ranges of 0.010 to 0.024 cm. Filaments melt-spun at 220°C had birefringence ranges of -0.25×10^{-3} to -1.02×10^{-3} and diameter ranges of 0.009 to 0.022 cm. Oven-drawn filaments (drawing temperatures ranging from 107°C to 120°C) had birefringence ranges of -0.19×10^{-3} to -1.28×10^{-3} and diameter ranges of 0.025 to 0.091 cm. For simplicity, filaments melt-spun at 180°C , 200°C , and 220°C will be designated as MS180, MS200, and MS220 respectively, and oven-drawn filaments will be designated as OD. Attempts will be made to correlate on single plots data from the above filaments whenever convenient.

Tensile Behavior

Figures 18-21 show the effect of birefringence on the stress-strain behavior of MS180, MS200, MS220, and OD, respectively. The behavior of MS180, MS200, and OD is very similar, as they all exhibit mainly brittle fracture. On the other hand, the MS220 shows well-defined yield points and ductile fracture. Detailed observations during tensile-testing revealed prominent necking, followed eventually by multiple splitting in all samples of MS220. In all the plots, the effect of birefringence on stress-strain behavior is quite evident.

The variation of Young's modulus with birefringence is illustrated in Figure 22. As expected, there is an increase in modulus with birefringence for all cases. Here, MS220 shows much higher modulus than the rest. MS180 and MS200 are again identical and show slightly higher moduli than OD. The plot seems to indicate that processing temperature affects the moduli of these filaments, with the temperature effect being more pronounced in MS220.

The variation of tensile strength with birefringence is shown in Figure 23. In all cases, tensile strength increases with increasing birefringence. However, again the difference in behavior is observed; the MS180, MS200, and OD show a monotonic increase in tensile strength with birefringence, while MS220 shows a decrease in the rate of tensile strength increase with birefringence at high birefringence levels. It is interesting to note that at the same birefringence level, OD shows the highest tensile strength, while MS220 shows the least. The plot also shows that the MS180 and MS200 are essentially identical.

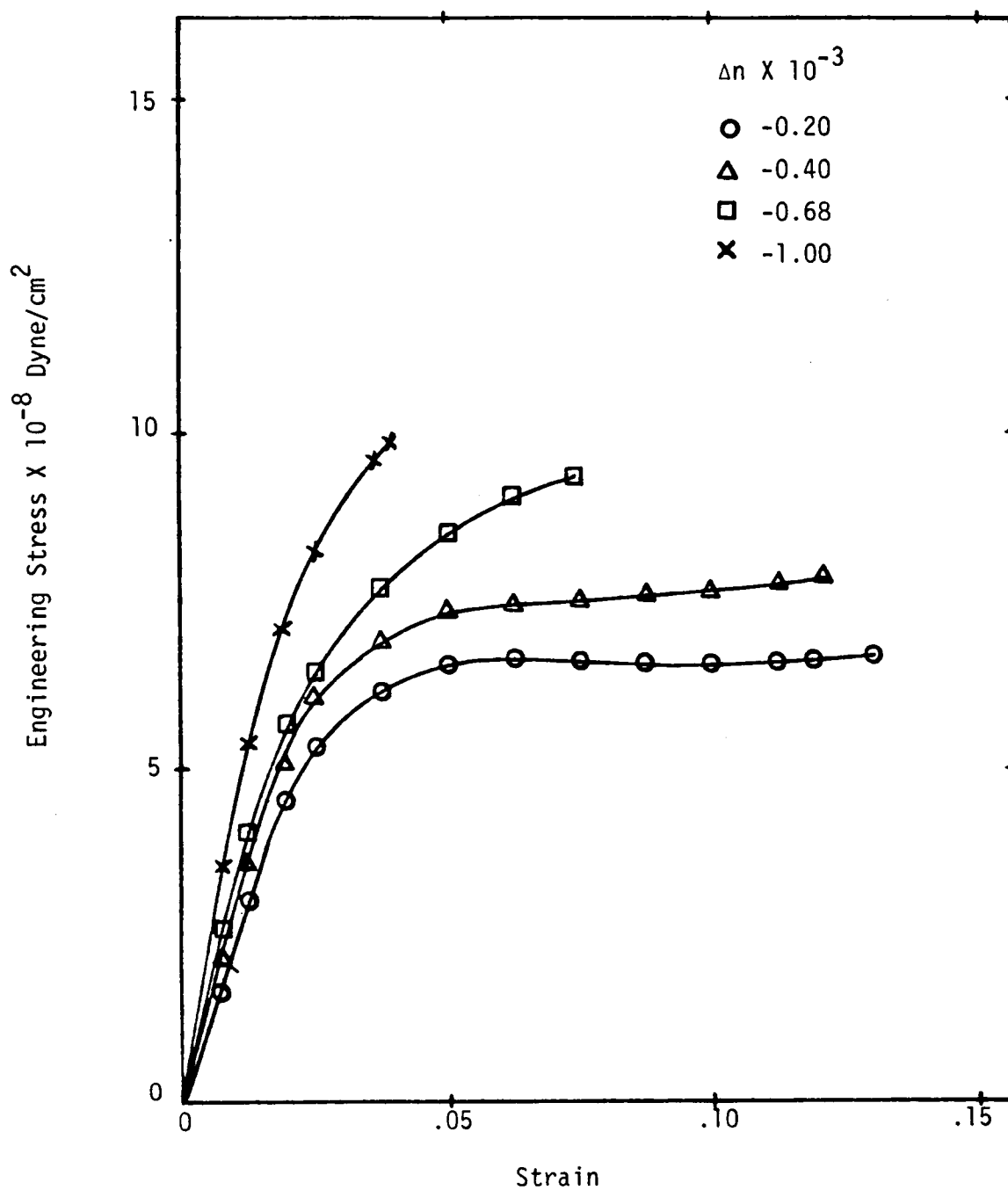


Figure 18: Effect of Birefringence on the Engineering Stress-Strain Relation of PMMA Filaments Melt Spun at 180°C.

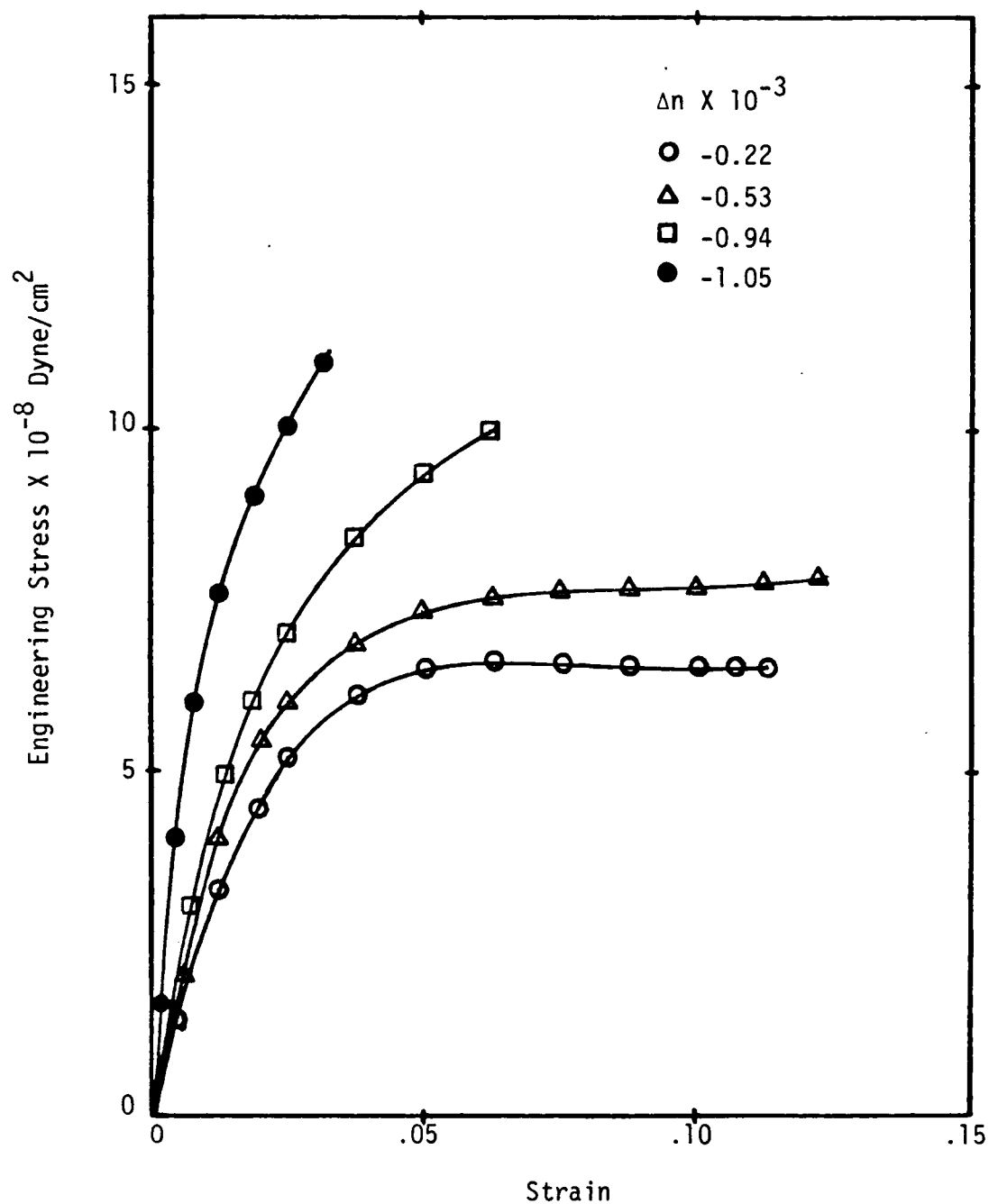


Figure 19: Effect of Birefringence on the Engineering Stress-Strain Relation of PMMA Filaments Melt Spun at 200°C.

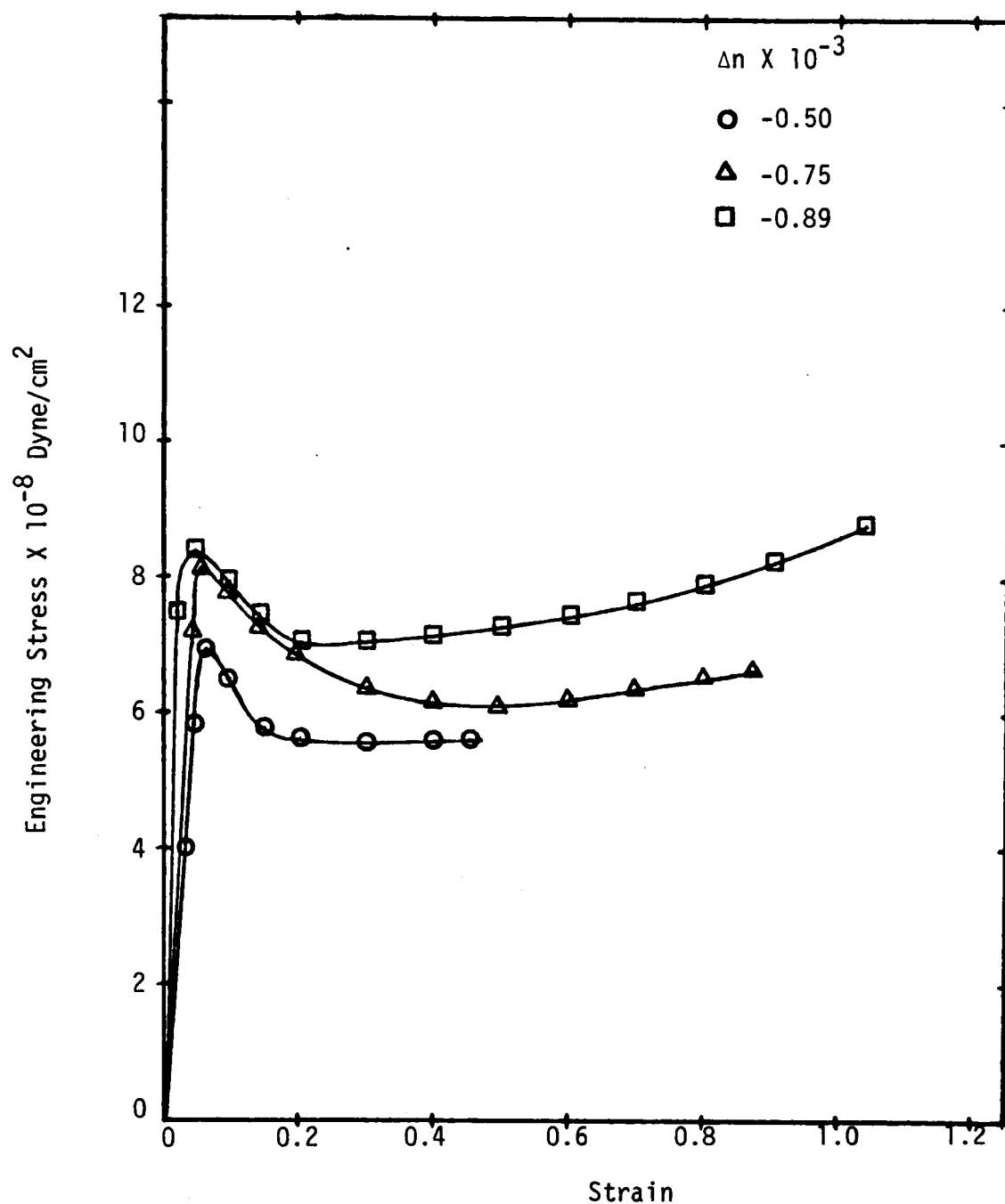


Figure 20: Effect of Birefringence on the Engineering Stress-Strain Relation of PMMA Filaments Melt Spun at 220°C.

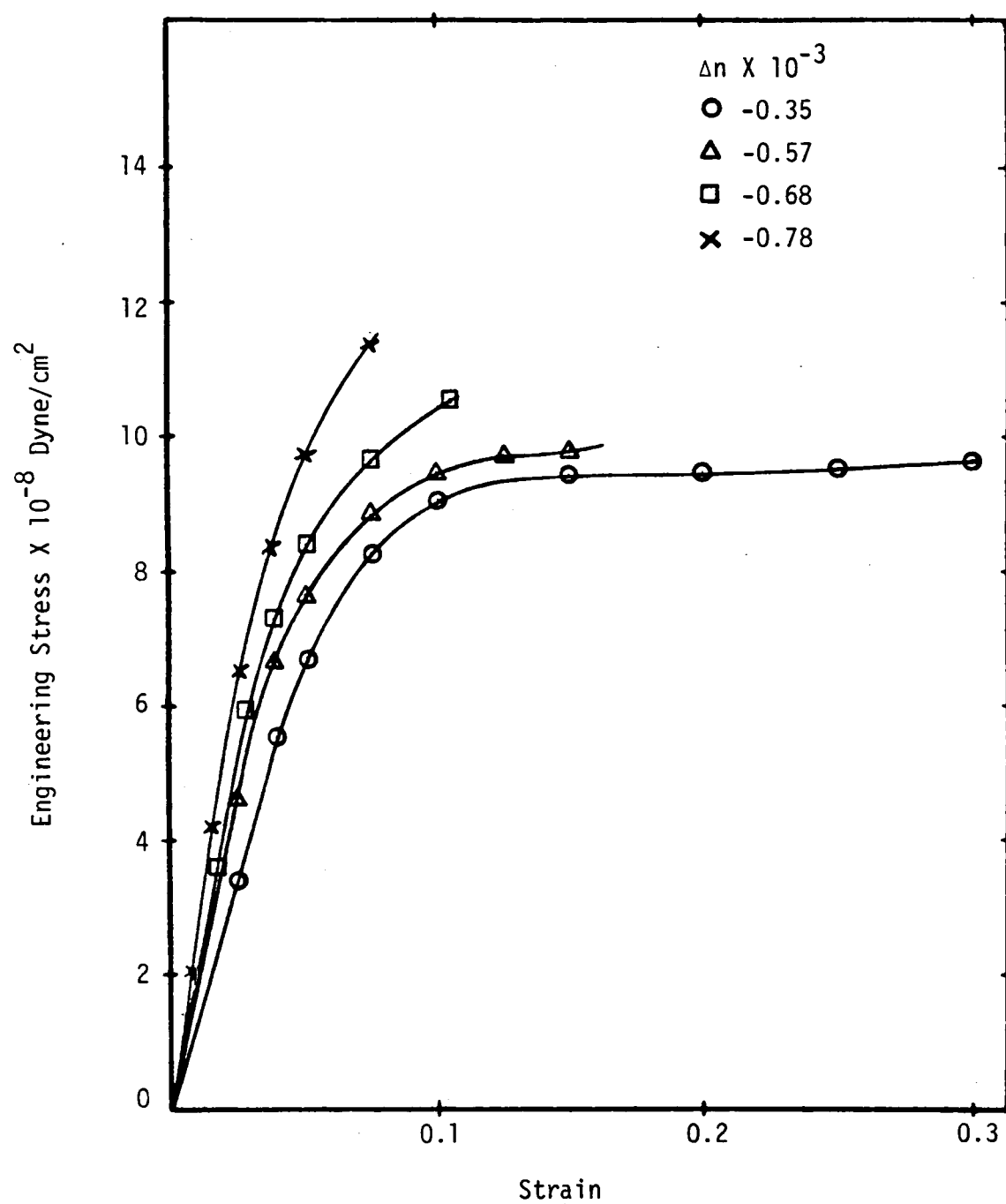


Figure 21: Effect of Birefringence on the Engineering Stress-Strain Relation of Oven-Drawn PMMA Filaments.

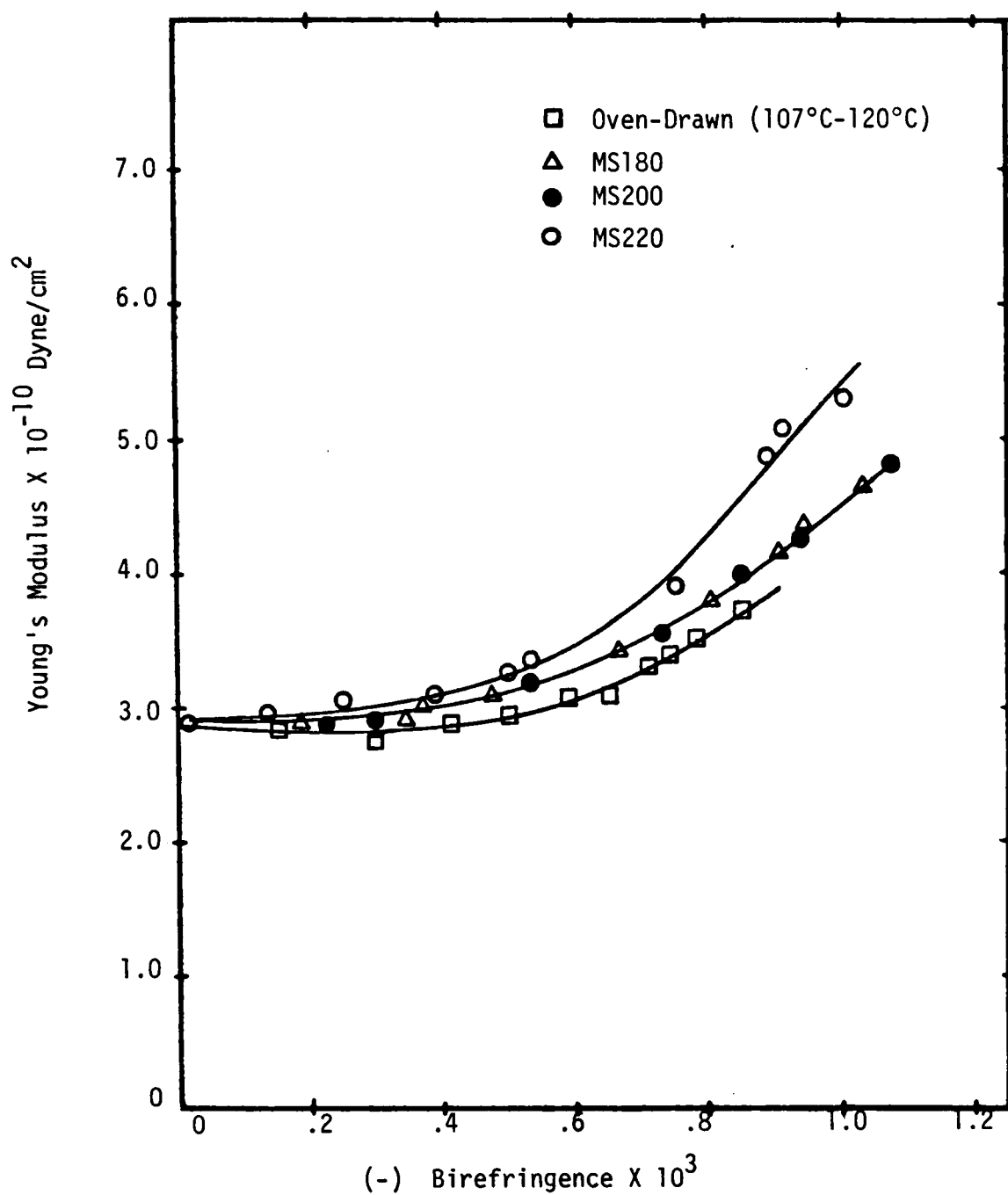


Figure 22: Effect of Processing Temperature on the Young's Modulus of PMMA Filaments as a Function of Birefringence.

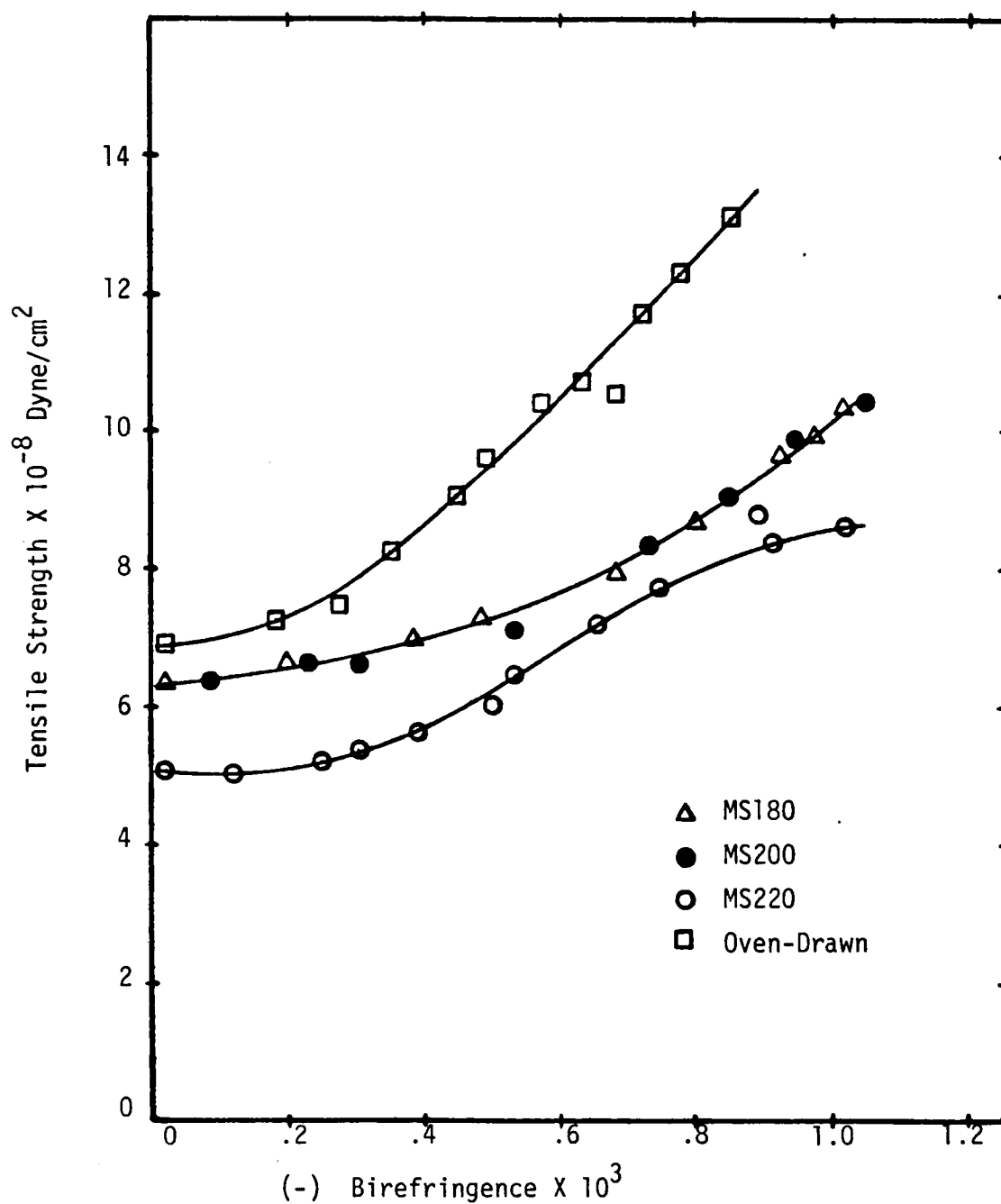


Figure 23: Variation of Tensile Strength With Birefringence for PMMA Filaments Melt Spun at 180°C, 200°C, 220°C, and Oven-Drawn at 107-120°C.

Figure 24 shows the correlation of birefringence with yield stress (obtained by Considere's construction whenever the yield point is not well defined). The curves for MS180, MS200, and OD show a monotonic increase in yield stress with birefringence, while that of MS220 exhibits a maximum and tends to decrease at higher birefringence levels. Again, data points for MS180 and MS200 fall on the same curve. Also at the same birefringence level, OD shows much higher yield stress than the others.

Dependence of elongation-to-break on birefringence is shown in Figure 25. For MS180, MS200, and OD, the elongation-to-break increases sharply with birefringence to a maximum of about 30%, and thereafter decreases drastically with increasing birefringence. There is a discontinuity at this maximum, and it occurs at a birefringence level of about -0.35×10^{-3} . Similar behavior has been observed for PS by Alfrey (2) and Kanetsuna and Tanabe (60,61). The latter author's study shows that in PS the discontinuity occurs at a birefringence level of about -2.0×10^{-3} , which is designated as brittle-to-ductile transition point. In contrast, MS220 shows a completely different behavior; the elongation-to-break increases steadily with birefringence to a maximum of about 104% and then starts decreasing without any discontinuity. In addition, MS220 in general has considerably higher elongation-to-break than the others. Again, it is of interest to note that MS180, MS200, and OD are almost identical in behavior.

Poisson's Ratio

Oriented filaments used in this measurement were prepared by over-drawing. The results are listed in the third column of Table V. There is little variation in extensional Poisson's ratio with birefringence,

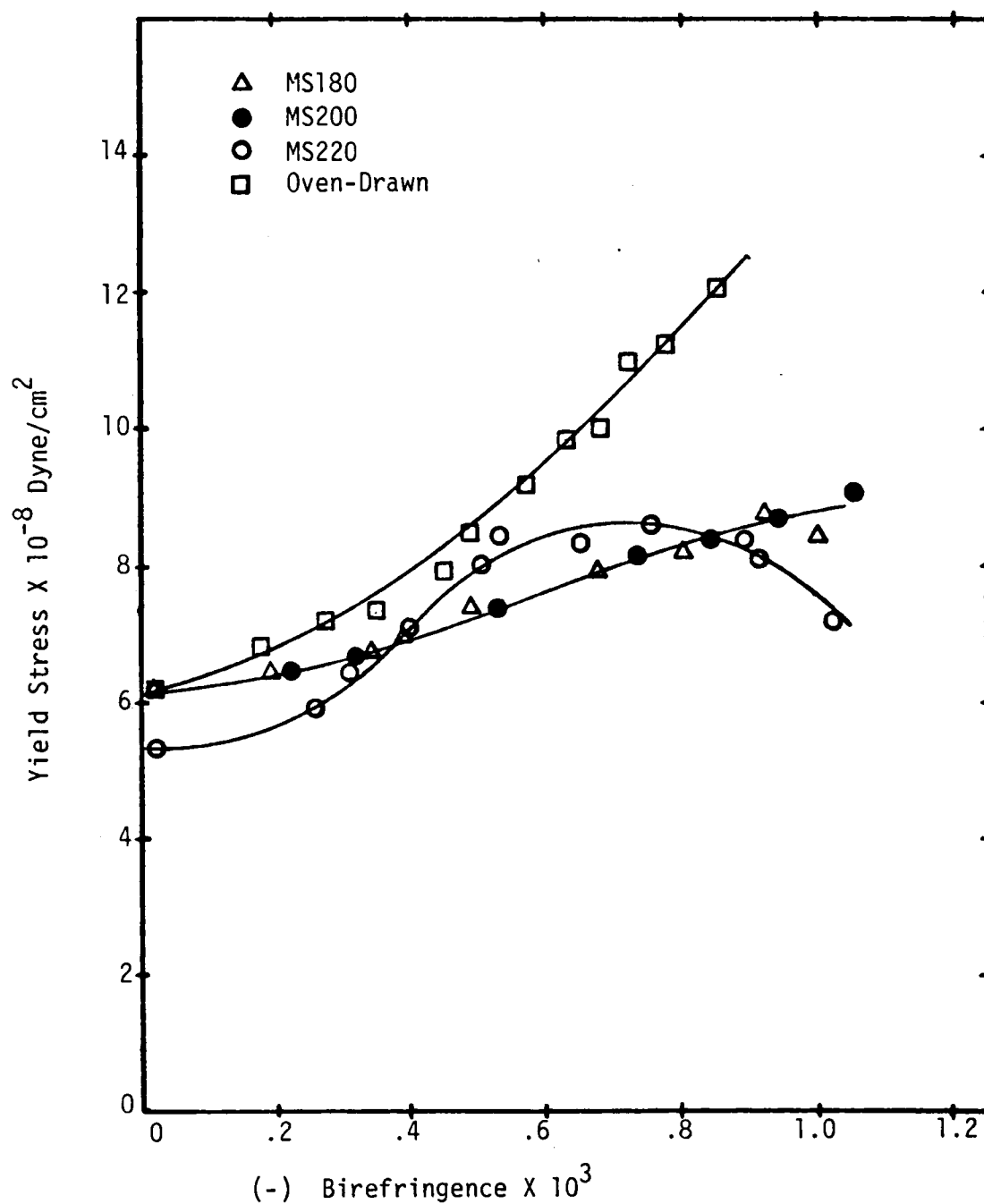


Figure 24: Effect of Birefringence on Yield Stress for MS180, MS200, MS220, and Oven-Drawn Filaments.

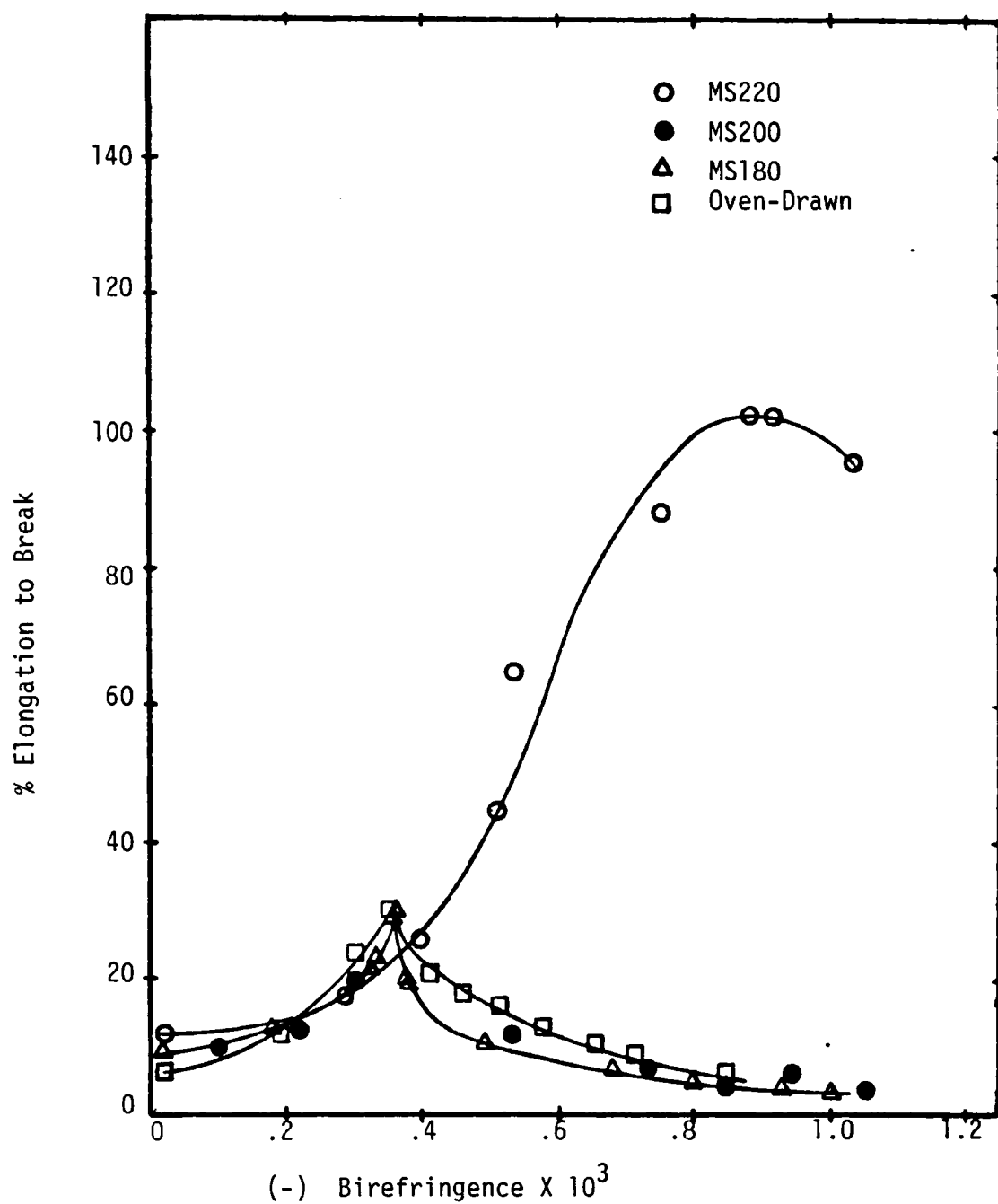


Figure 25: Effect of Birefringence on the Percent Elongation to Break of PMMA Filaments Melt-Spun at 180°C, 200°C, 220°C, and Oven-Drawn at 107-120°C.

TABLE V
SOME MECHANICAL PROPERTIES OF OVEN-DRAWN
FIBERS OF PMMA*

Diameter (cm)	$-\Delta n$ ($\times 10^3$)	Extensional Poisson's Ratio	E ($\times 10^{-10}$ dyne/cm ²)	G ($\times 10^{-10}$ dyne/cm ²)
0.067	0.02	0.34	2.90	1.09
0.066	0.49	0.39	3.00	1.12
0.064	0.56	0.39	3.05	1.21
0.067	0.57	0.38	3.05	1.16
0.064	0.59	0.32	3.08	1.24
0.065	0.63	0.39	3.10	1.25
0.063	0.65	0.34	3.10	1.31
0.065	0.68	0.38	3.20	1.30
0.063	0.72	0.34	3.30	1.33
0.066	0.74	0.38	3.40	1.32
0.063	0.78	0.40	3.50	1.36
0.063	0.85	0.44	3.75	1.35

*Drawing temperatures: 110-112°C.

but this variation doesn't seem to suggest any correlation between Poisson's ratio and birefringence. The apparent variation could be due to experimental error. However, the values are all consistently lower than 0.5, the value which would correspond to axial incompressibility.

Torsional Modulus

The filaments were prepared by oven-drawing with diameters ranging from 0.063 to 0.067 cm. The results are listed in Table V, together with results of both Young's modulus and Poisson's ratio. The effect of birefringence on torsional modulus is graphically shown in Figure 26, and it shows that there is a slight increase in torsional modulus at higher birefringence levels. The effect of filament diameter on torsional modulus is also illustrated in Table VI. It clearly shows that within each of the birefringence levels, the torsional modulus increases with decreasing filament diameter.

Discussion

The mechanical properties of the oriented PMMA filaments prepared by melt-spinning and oven-drawing are, in general, dependent upon their levels of birefringence. Specifically, the elastic modulus, tensile strength, and yield stress all increase with birefringence. There is a slight increase in torsional modulus with birefringence, but in this case the extreme sensitivity of the measurement to filament diameter makes it difficult for one to assess the true effect of birefringence on the torsional modulus. The apparent lack of correlation between extensional Poisson's ratio and birefringence is not exactly unexpected. This is because almost all methods of measurement of Poisson's ratio are characterized by large errors. These are, in part, due to non-uniformity in

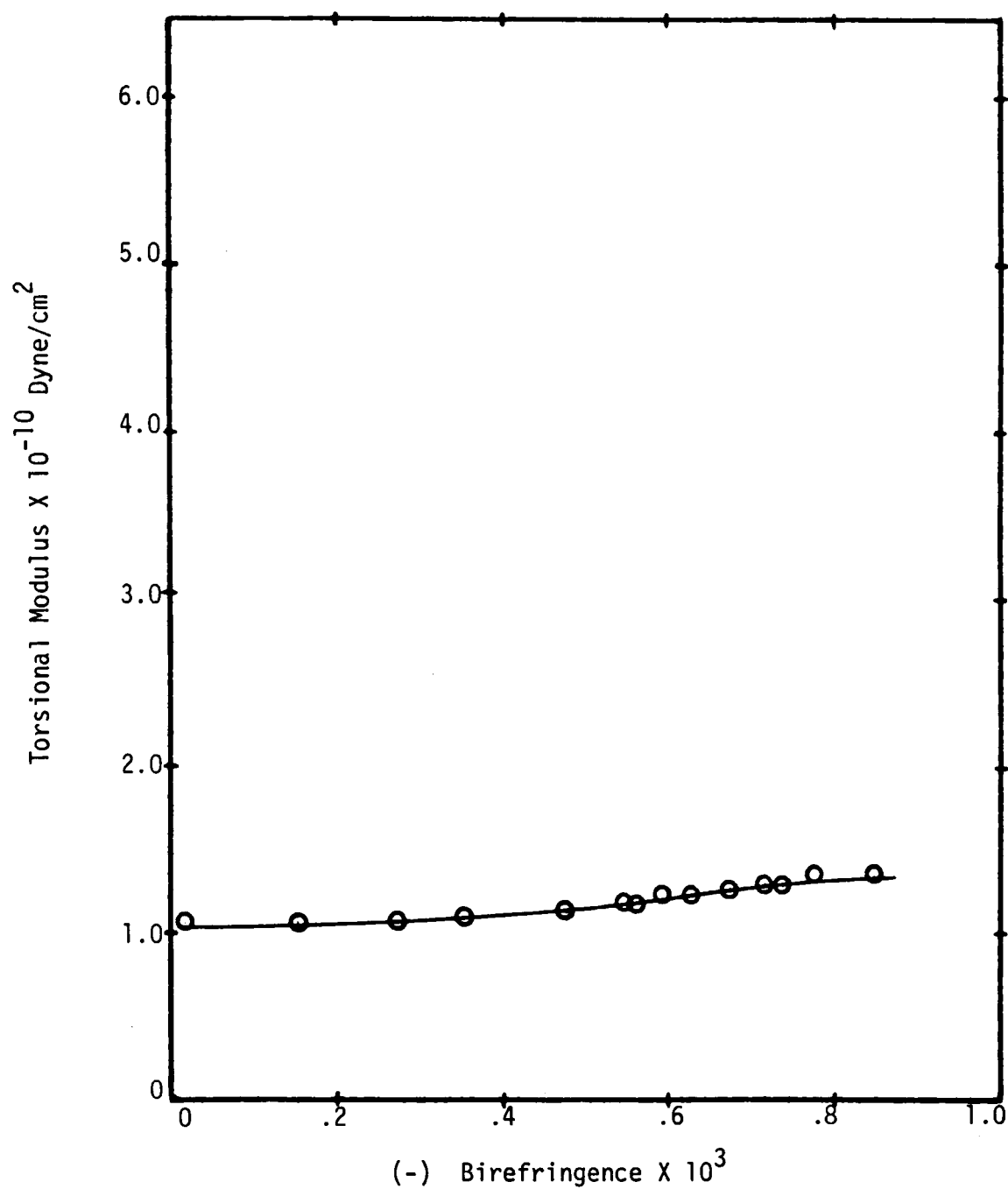


Figure 26: Variation of Torsional Modulus with Birefringence for PMMA Filaments Oven-Drawn at Temperatures 107-120°C.

TABLE VI
DEPENDENCE OF TORSIONAL MODULUS ON FIBER DIAMETER
FOR OVEN-DRAWN FIBERS OF PMMA

Birefringence - ($\Delta n \times 10^3$)	Diameter (cm)	Torsional Modulus ($\times 10^{-10}$ dyne/cm ²)
0.66	0.071	1.15
0.66	0.068	1.17
0.66	0.061	1.21
0.66	0.037	4.73
0.70	0.071	1.13
0.70	0.066	1.20
0.70	0.042	3.76
0.58	0.070	1.27
0.58	0.057	1.81
0.58	0.035	2.52

diameter along the filament length, resulting in non-uniform deformation in the test piece.

The curious mechanical behavior of MS220 is indicative of different structural changes resulting from thermal degradation. The higher the processing temperature, the more the degradation, because increases in temperature are noted to increase the rate of bond rupture and to decrease the macroscopic strength (28,74). The overall modifications that can take place during processing involve destruction of supermolecular structures, a change in molecular weight and its distribution, crosslinking, and the formation of new functional groups along or at the ends of the chain. Also, thermal degradation can result in formation of flaws which may vary in size, sharpness or radius, distance from each other, and orientation with respect to the stretch direction (115). During tensile deformation, many of these flaws are able to share the strain, and this results in ductile extensibility. Stated another way, degradation can introduce localized stress in the filament, and this results in localized dilation and increase in entropy, which, in turn, causes a tremendous shortening in relaxation time, permitting localized relaxation instead of fracture (79). All these could account for the ductile behavior of MS220.

The slight increase in torsional modulus with birefringence is consistent with the finding reported by Ward (130). From the graph (see Figure 26), the torsional modulus of a perfectly isotropic filament is about 1.09×10^{10} dyne/cm², which compares favorably with the value of 1.06×10^{10} dyne/cm² reported by Kashiwagi and co-workers (63). It must be emphasized again that torsional measurements are subject to large errors. This is due to slight variations in the radius along a length

of filament, which leads to a larger variation in the torsional modulus which depends on the fourth power of the radius.

It can be inferred from the various experiments on the mechanical behavior of the filaments that the most important phenomenological difference between the MS220 filaments and all the others relates to the mode of yielding. MS220 filaments exhibit non-homogeneous yielding via necking, while the MS180, MS200, and OD filaments all exhibit homogeneous yielding. This could explain why MS180, MS200, and OD filaments, although prepared at different temperatures, have identical mechanical behaviors. The non-homogeneous yielding in MS220 arises from stress intensification around flaws or micro-heterogeneities. The yield stress is first attained in the region of the flaw, and then a neck can form and propagate, resulting in ductile extensibility.

Quenched Filaments

To investigate the effects of thermal stresses resulting from rapid cooling, some mechanical properties of PMMA filaments extruded at different barrel temperatures into an ice bath were examined. Graphs of $\Delta T (= T_b - T_o)$ and birefringence are plotted against the various mechanical properties. T_b and T_o are the extrusion and ice bath temperatures, respectively.

Figure 27 shows the effect of ΔT and birefringence on the stress-strain behavior of the ice-quenched PMMA filaments. The plot indicates that filaments extruded at 170°C and 180°C exhibit ductile fracture behavior similar to that of MS220 filaments. Also, as the extrusion temperature increases, the birefringence increases; however, the fracture behavior tends to be brittle.

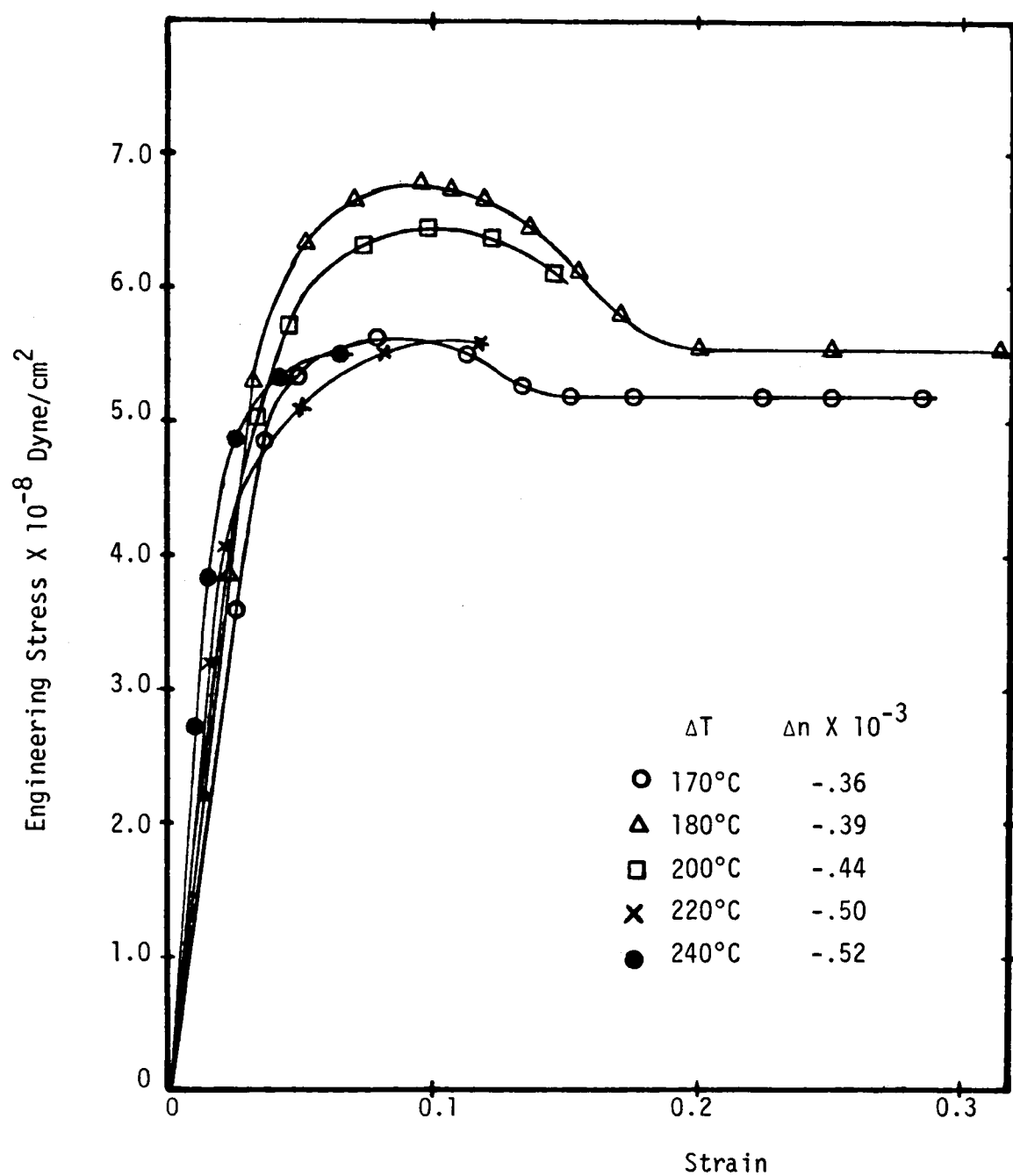


Figure 27: Effect of Extrusion Temperature on Stress-Strain Relation of PMMA Filaments Extruded Directly into Ice Water Bath.

The effect of quenching on Young's modulus is shown in Figure 28. There is a slight increase in modulus with increasing ΔT and birefringence. The result is consistent with that obtained for MS180, MS200, MS220, and OD filaments, where the Young's modulus was found to increase with increasing processing temperature and birefringence. The modulus values in this case are, however, smaller than those of the above mentioned filaments.

The tensile strength and yield stress are plotted against ΔT in Figure 29. The plot shows the yield stress is consistently greater than the corresponding tensile strength for ΔT values up to 200°C, beyond which the trend reverses. The important observation in this plot is that ΔT and, consequently, birefringence changes, do not reveal much significant change in both tensile and yield stress. Thus, the seemingly observed differences could be due to experimental errors.

Figure 30 illustrates the effect of quenching on elongation-to-break. The percent elongation-to-break decreases with increasing ΔT and birefringence. This behavior is identical to that observed for the melt-spun and oven-drawn filaments for birefringence values greater than -0.35×10^{-3} , with the exception of MS220. The effects of ΔT and birefringence on all the above mentioned mechanical properties are listed in Table VII for convenient comparison. It can be seen that even though there is a significant amount of birefringence development arising from the thermal stresses accompanying such rapid cooling, the mechanical properties of the quenched filaments are, in general, little affected. Broutman and Krishnakumar (22) have reported that in PMMA, although there is a creation of a different metastable glassy structure (expanded free volume) due to quenching, the impact strength is not influenced by quenching.

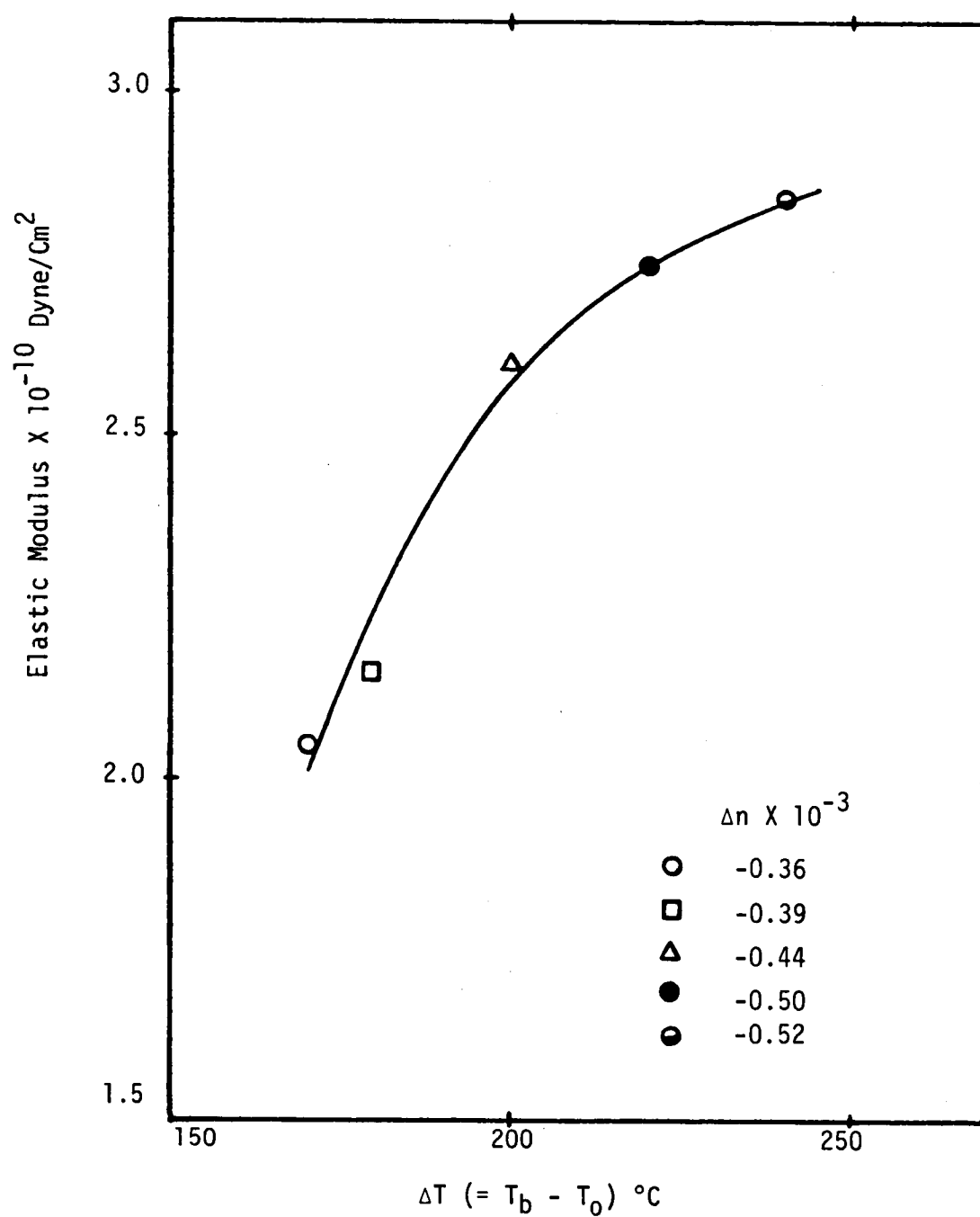


Figure 28: Effect of Spinning Temperature on Young's Modulus of PMMA Filaments Extruded Directly into Ice Bath.

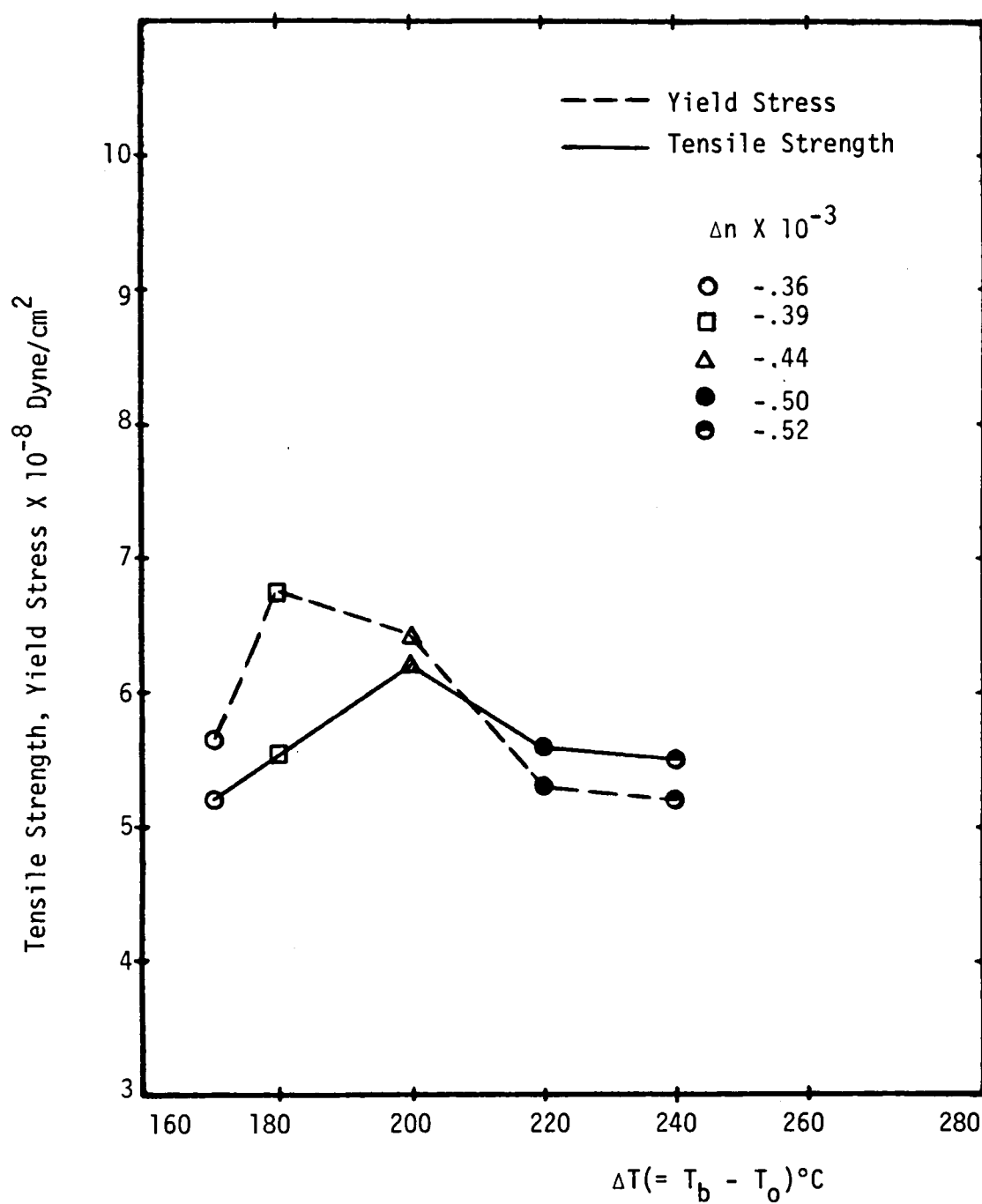


Figure 29: Effect of Spinning Temperature on Tensile Strength and Yield Stress of PMMA Filaments Extruded Directly into Ice Water Bath.

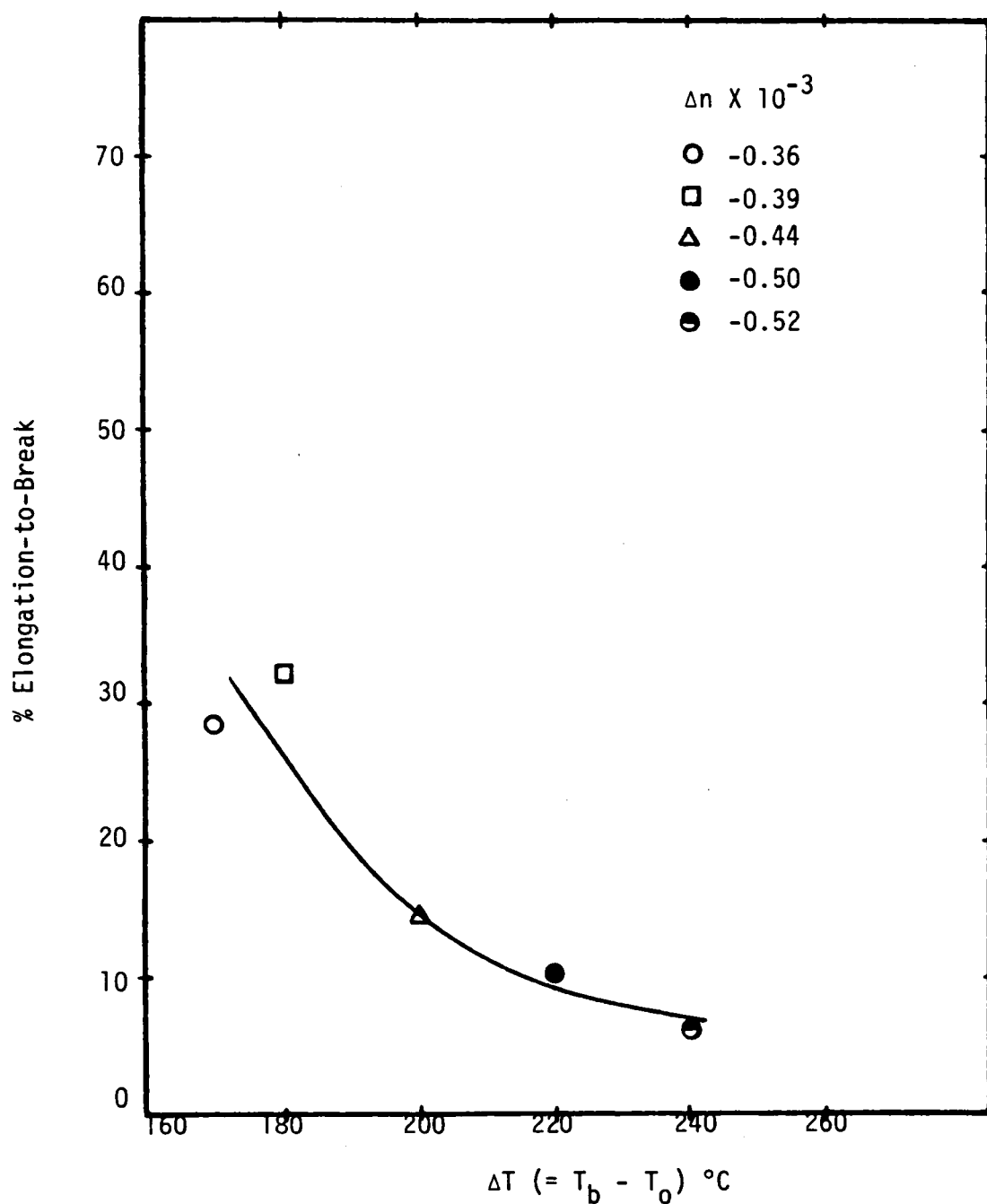


Figure 30 : Effect of Spinning Temperature on Percent Elongation-to-Break of PMMA Filaments Extruded Directly into Ice Bath.

TABLE VII
EFFECT OF RAPID QUENCHING ON BIREFRINGENCE AND MECHANICAL PROPERTIES
OF PMMA FILAMENTS

$\Delta T, ^\circ\text{C}$ ($T_b - T_o$)	Δn_3 ($\times 10^{-3}$)	Young's Modulus ($\times 10^{-10}$ dyne/cm ²)	Tensile Strength ($\times 10^{-8}$ dyne/cm ²)	Yield Stress ($\times 10^{-8}$ dyne/cm ²)	Elongation- to-Break (%)
170	-0.36	2.05	5.20	5.62	28.5
180	-0.39	2.12	5.55	6.78	32.0
200	-0.44	2.60	6.20	6.45	14.0
220	-0.50	2.77	5.60	5.30	10.0
240	-0.52	2.85	5.50	5.20	6.0

B. COMPARISON AND CONCLUSIONS

In order to investigate the separate and combined effects of orientation birefringence and thermal stress on the mechanical properties of filaments studied, attempts have been made to correlate the properties of the various filaments on single plots. (Figure 31 shows the effect of birefringence and thermal stress on Young's modulus of melt-spun, oven-drawn, and quenched PMMA filaments, together with the effect of birefringence on torsional modulus and Poisson's ratio. The behavior of quenched filaments indicates that Young's modulus increases with thermal stress. For the same birefringence level, the melt-spun filaments exhibit comparatively higher moduli than oven-drawn filaments. This seems to suggest that thermal stress effects in melt-spun filaments are greater than in oven-drawn filaments. The Poisson's ratio and torsional modulus are little affected by birefringence; therefore, thermal stress effect, if any at all, will be little. The behavior of MS220, as stated before, is partly due to thermal degradation.

The effect of birefringence and thermal stress on tensile strength of the filaments is illustrated in Figure 32. The behavior of the quenched filaments implies that higher thermal stress values tend to decrease tensile strength. Since oven-drawn filaments comparatively have much higher tensile strength than melt-spun filaments, it can be inferred that thermal stresses associated with melt-spun filaments are much higher than in oven-drawn filaments. Even the much lower tensile strength for MS220 is consistent with the fact that under identical cooling conditions, the higher the processing temperature, the higher the thermal stress.

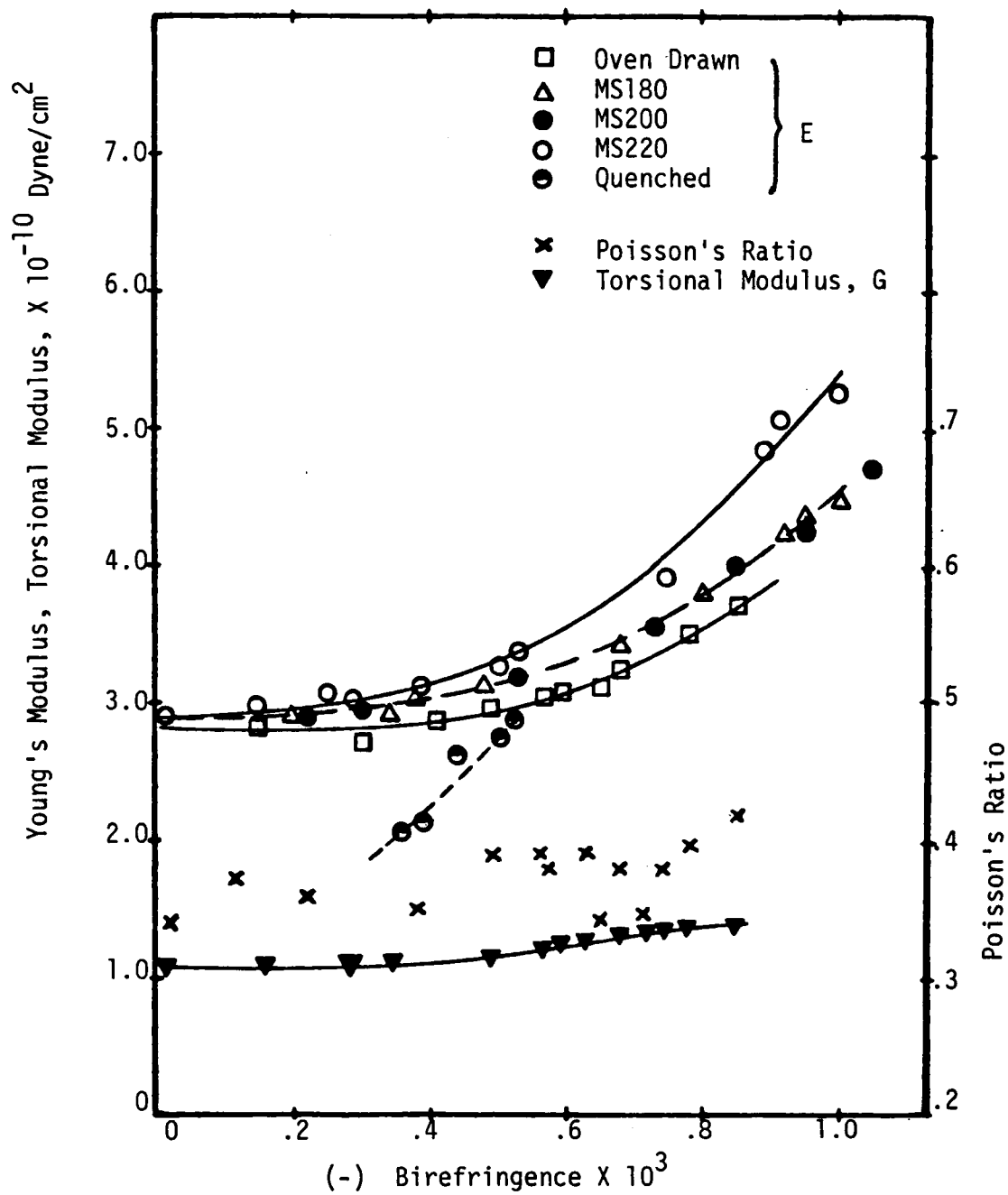


Figure 31: Effect of Birefringence on Young's Modulus, Torsional Modulus, and Poisson's Ratio (in the case of Quenched Filaments, Δn reflects Thermal Stress).

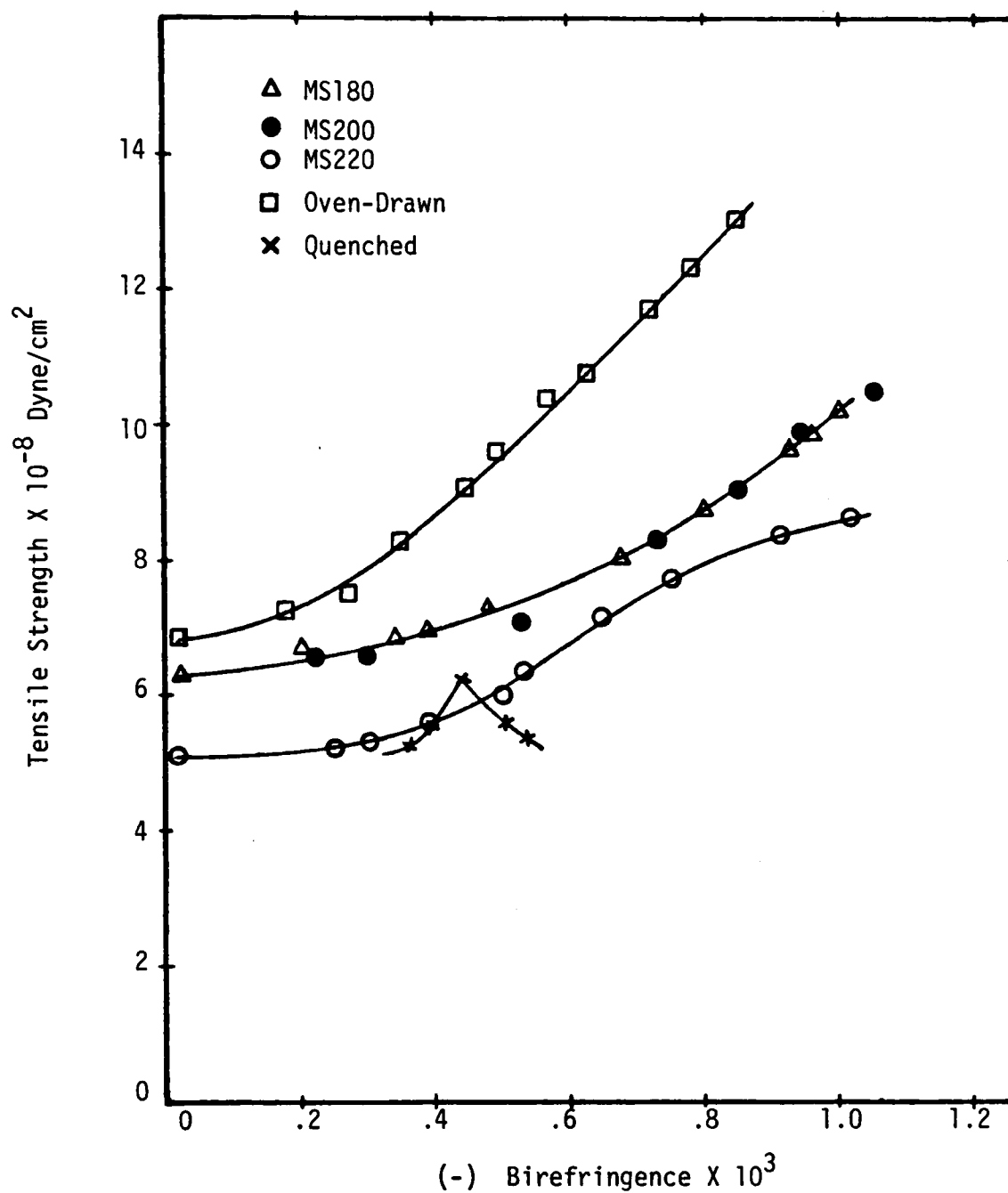


Figure 32: Effect of Birefringence and Thermal Stress on Tensile Strength of the Different Filaments.

The effect on yield stress is shown in Figure 33. Here again, the behavior of the quenched filaments suggests that appreciable thermal stress tends to reduce yield stress. The melt-spun filaments consistently show much lower yield stress than oven-drawn filaments. However, the steady increase in yield stress with birefringence for melt-spun filaments can be attributed to the birefringence resulting from molecular orientation. The apparent sigmoidal behavior of MS220 can be indicative of structural changes resulting from thermal degradation.

Figure 34 is the summary of the effect of birefringence and thermal stress on the percent elongation-to-break. It shows that thermal stress decreases the elongation-to-break and that it affects the melt spun filaments (MS180, MS200) more than the oven drawn filaments.

The following conclusions can be drawn from the behavior of all the different filaments studied:

1. Thermal stress results from the combination of high processing temperature and rapid cooling to room temperature. Thus, in melt-spinning and oven-drawing, thermal stress cannot be entirely ignored.
2. The effect of thermal stress in these filaments is to increase Young's modulus and to decrease both tensile strength and yield stress. The Poisson's ratio and torsional modulus are relatively unaffected by thermal stress.

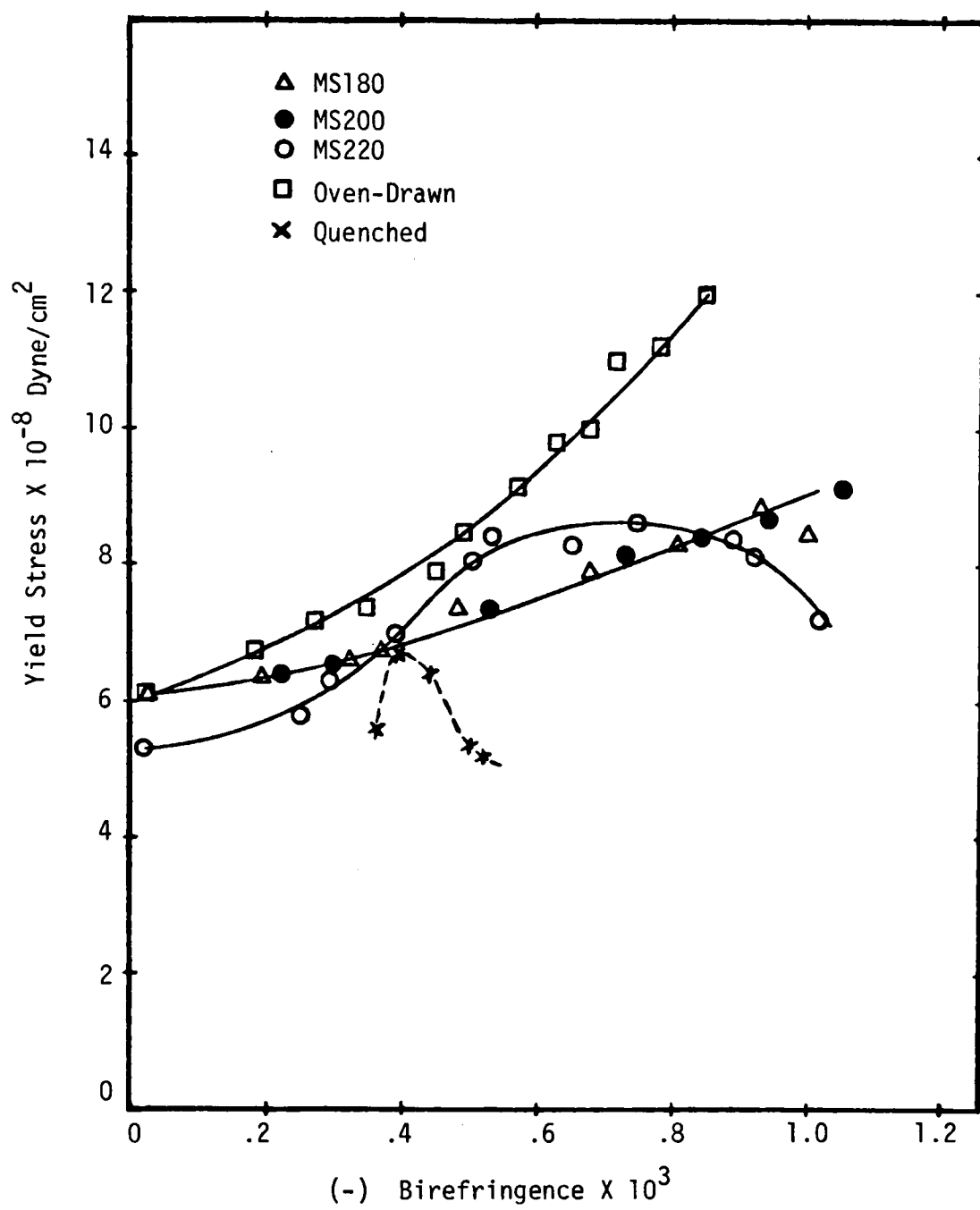


Figure 33: Effect of Birefringence and Thermal Stress on Yield Stress of the Different Filaments.

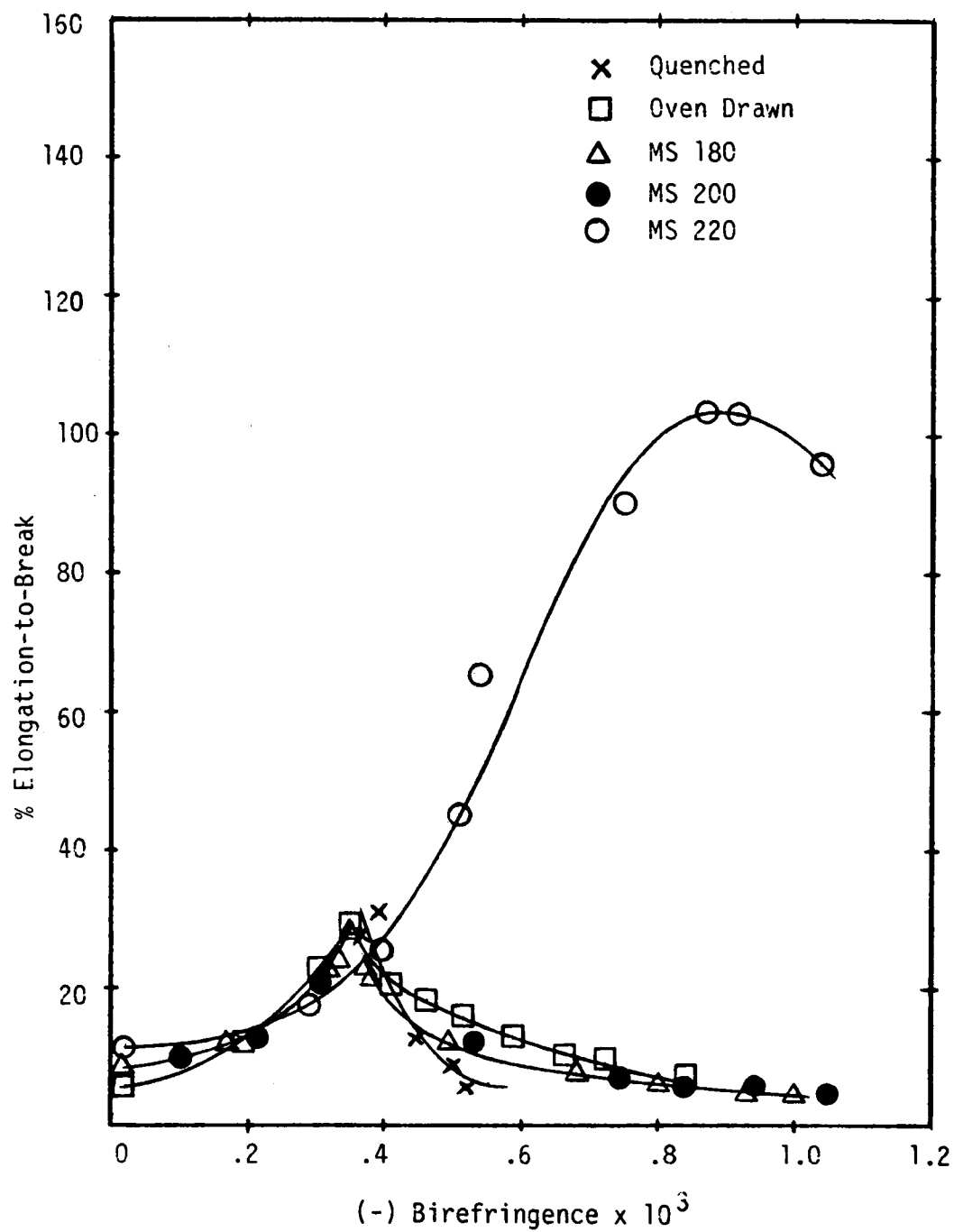


Figure 34: Effect of Birefringence on the Percent Elongation-to-Break of All the Differently Prepared PMMA Filaments.

3. Most importantly, the properties of oven-drawn filaments are mainly due to molecular orientation (orientation birefringence), while those of melt-spun filaments are as a result of both molecular orientation and thermal stress.

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APPENDICES

APPENDIX A

THE TEMPERATURE DEPENDENCE OF STRESS OPTICAL COEFFICIENT

The stress-optical coefficient of many polymers varies with temperature. Figures A-1 to A-7 show the variation of the stress-optical coefficient with temperature for some selected polymers.

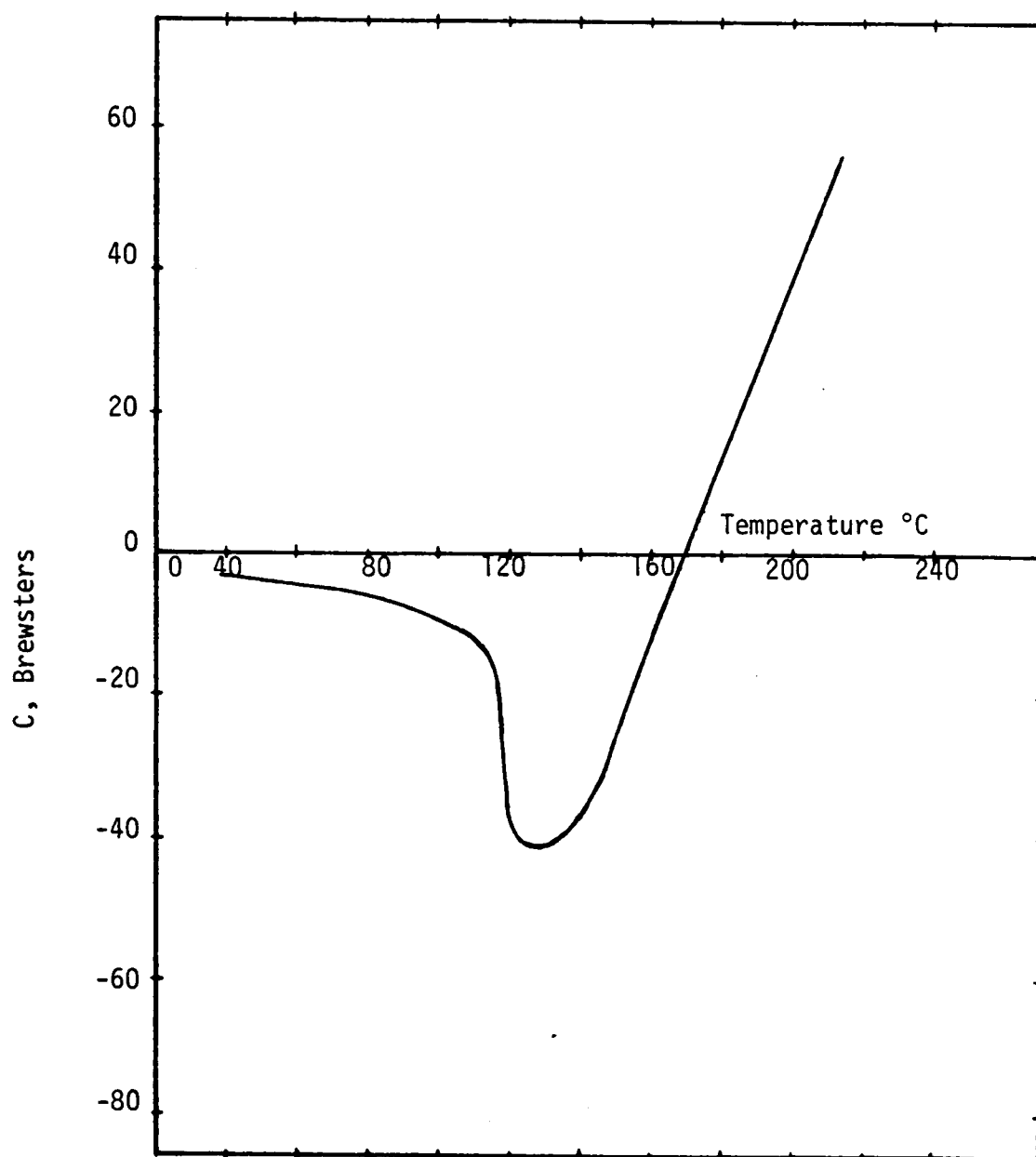


Figure A-1: Variation of Stress-Optical Coefficient of PMMA on Temperature.

Source: Tsvetkov, V. N. and L. N. Verkhovina, Sov. Phys.-Tech. Phys., 3, 87 (1958).

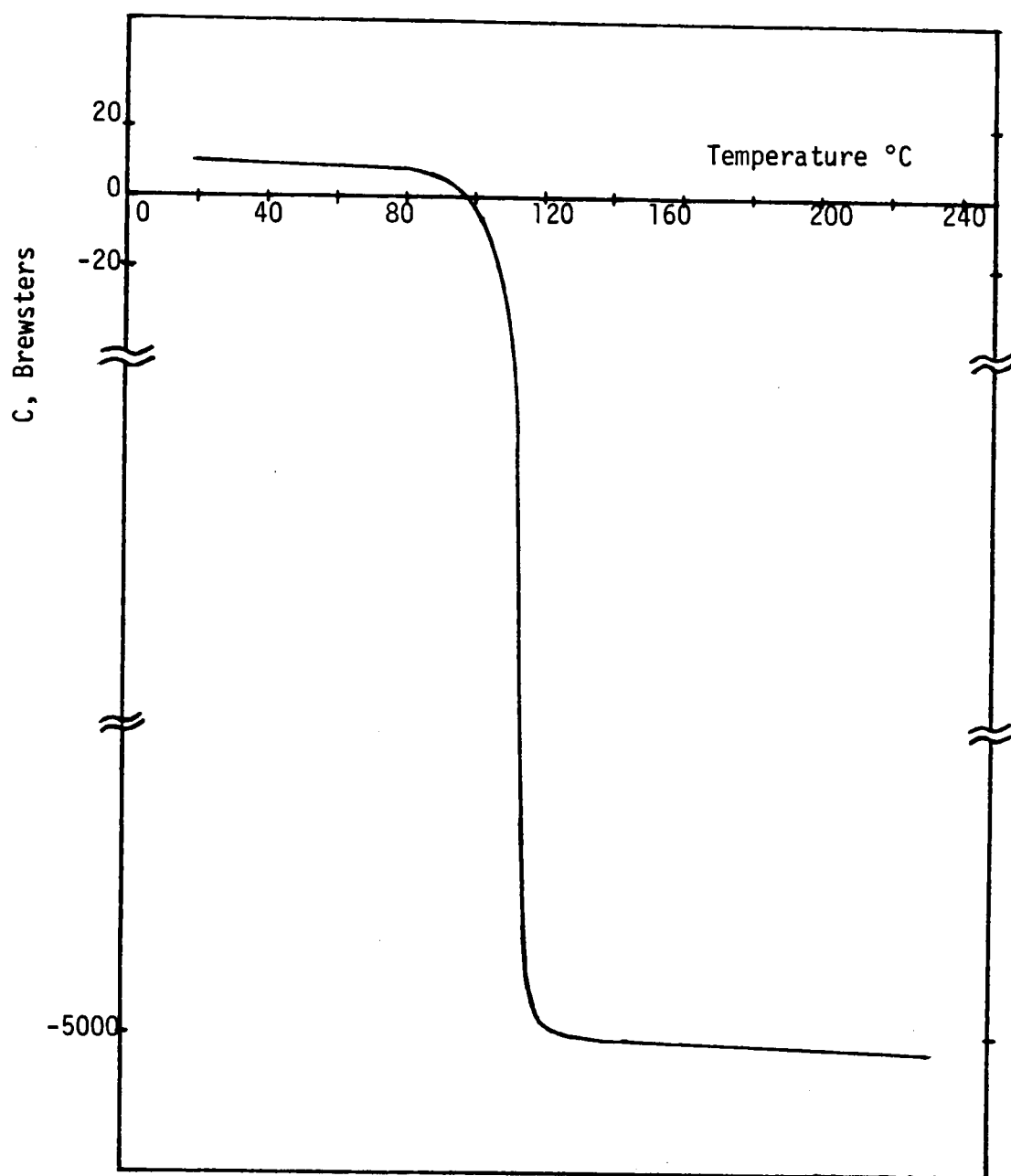


Figure A-2: Variation of Stress-Optical Coefficient of Polystyrene with Temperature.

Source: Andrews, R. D., R. Houwink and H. K. Decker, in R. Houwink and H. K. Decker (Eds.), *Elasticity, Plasticity and Structure of Matter*, 3rd Edn., Cambridge Univ. Press (1971).

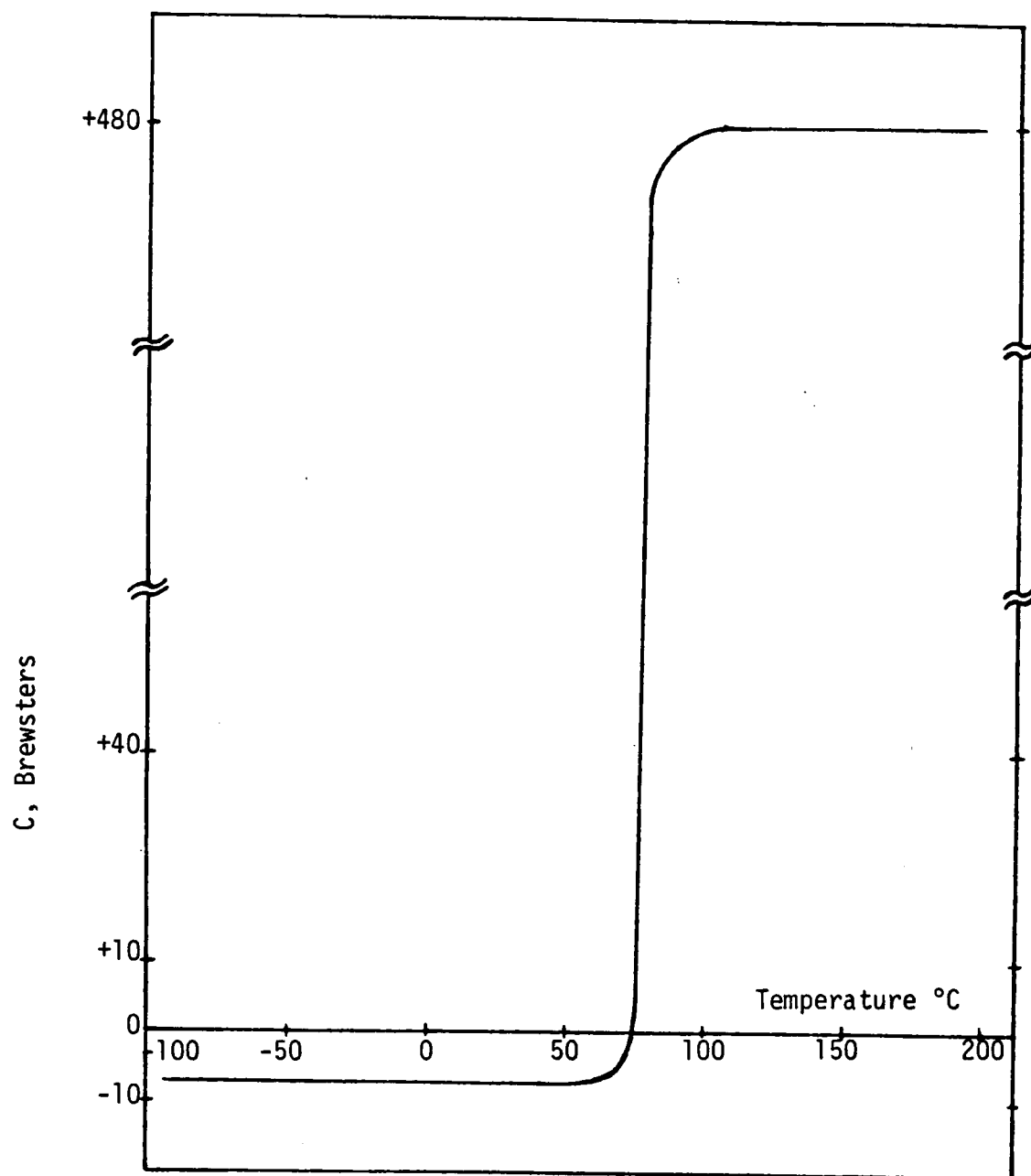


Figure A-3: Variation of Stress-Optical Coefficient of PVC (Unplasticized) with Temperature.

Sources: Andrews, R. D. and Y. Kazama, J. Appl. Phys. 39, 4891 (1968). Wales, J. L. S., The Application of Flow Birefringence to Rheological Studies of Polymer Melts, Delft Univ. Press (1976).

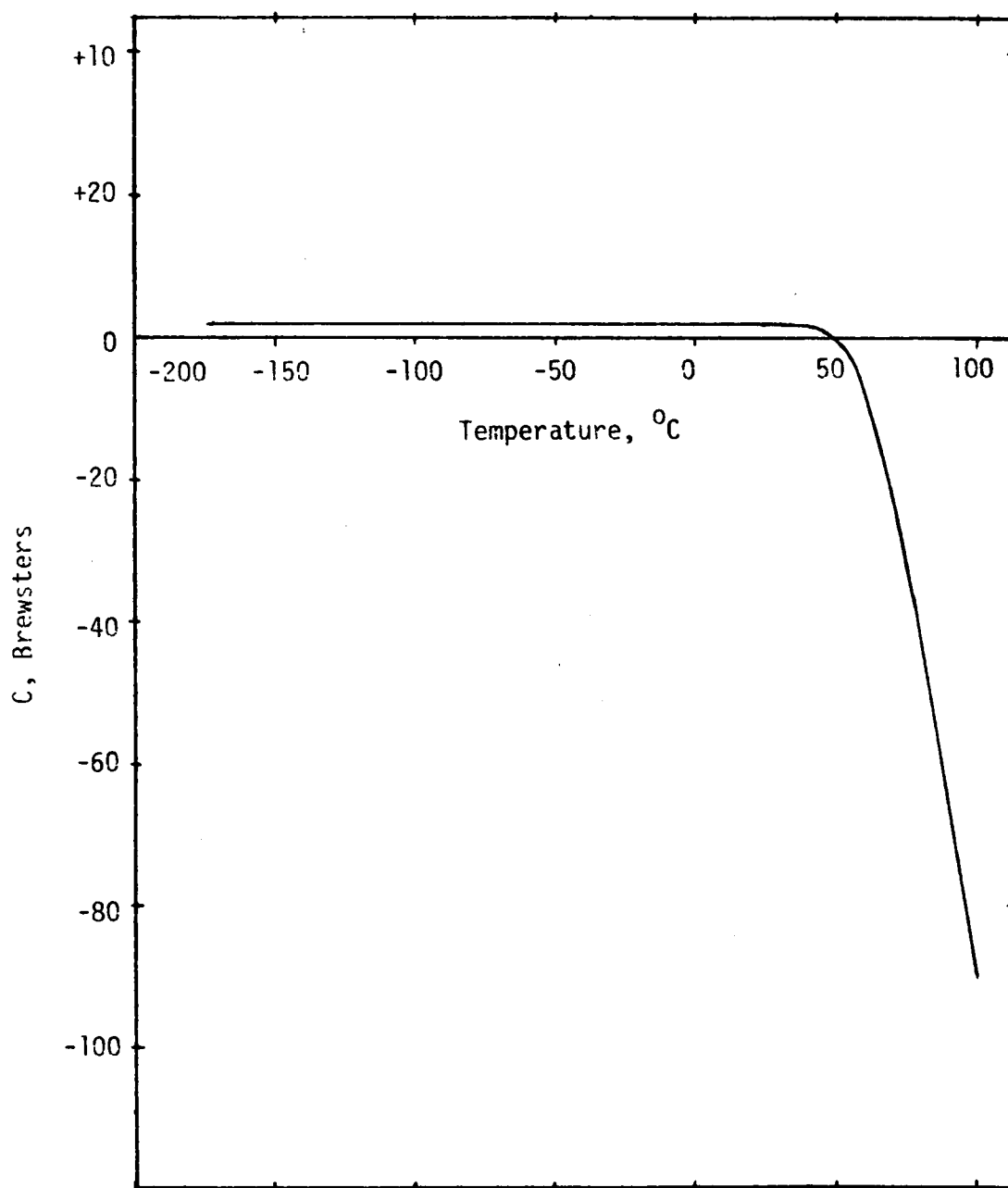


Figure A-4. Temperature Dependence of Stress-Optical Coefficient for Acrylonitrile/Vinyl Acetate (93/7) Copolymer.

Source: Andrews, R. D. and R. M. Kimmel, J. Appl. Phys., 35, 3194 (1964).

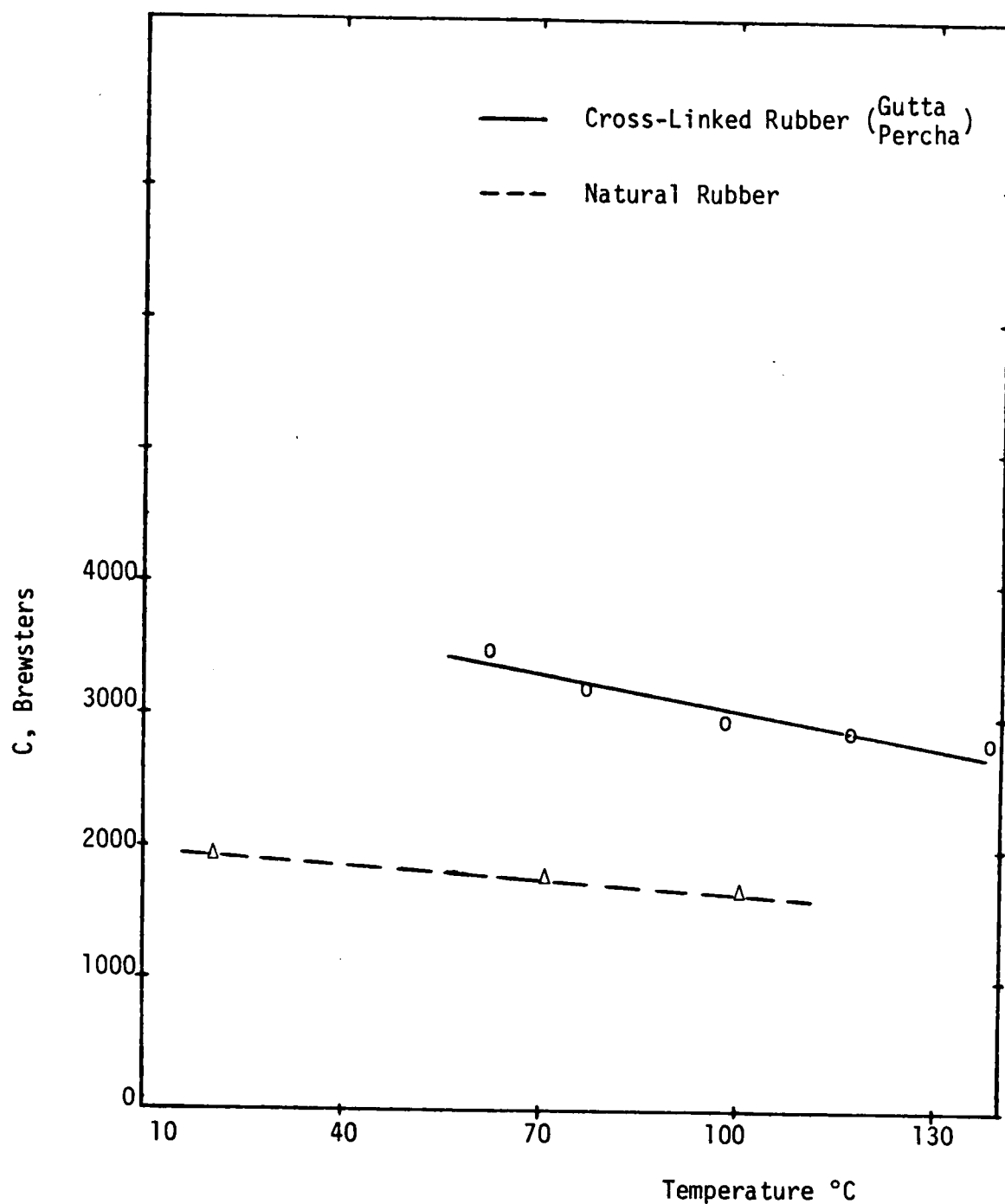


Figure A-5: Variation of Stress-Optical Coefficient of Natural Rubber and Cross-Linked Rubber with Temperature.

Source: Saunders, D. W., Trans. Farad. Soc., 52, 1414 (1956).

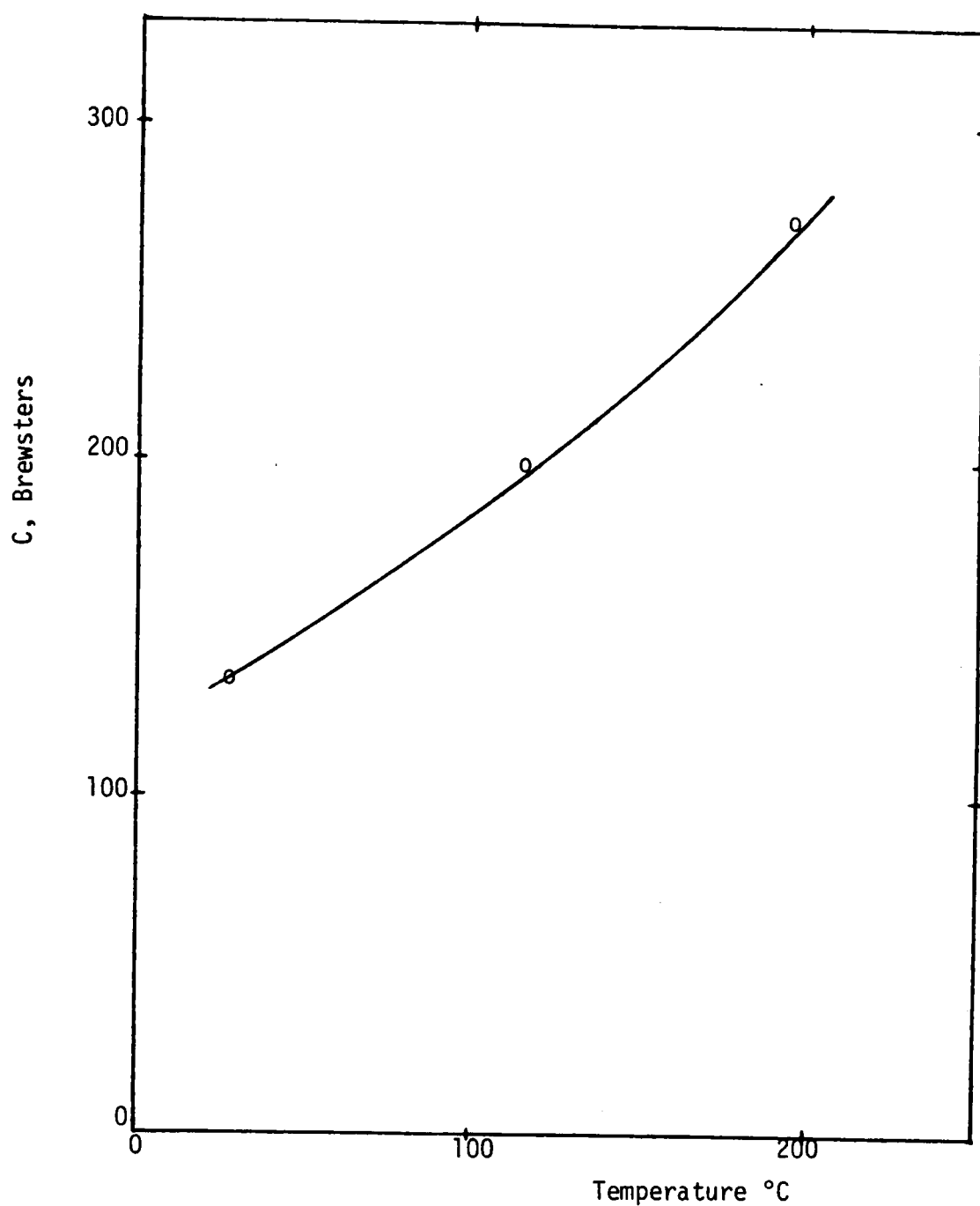


Figure A-6: Variation of Stress-Optical Coefficient of Polydimethylsiloxane with Temperature.

Source: Wales, J. L. S., The Application of Flow Birefringence to Rheological Studies of Polymer Melts, Delft Univ. Press (1976).

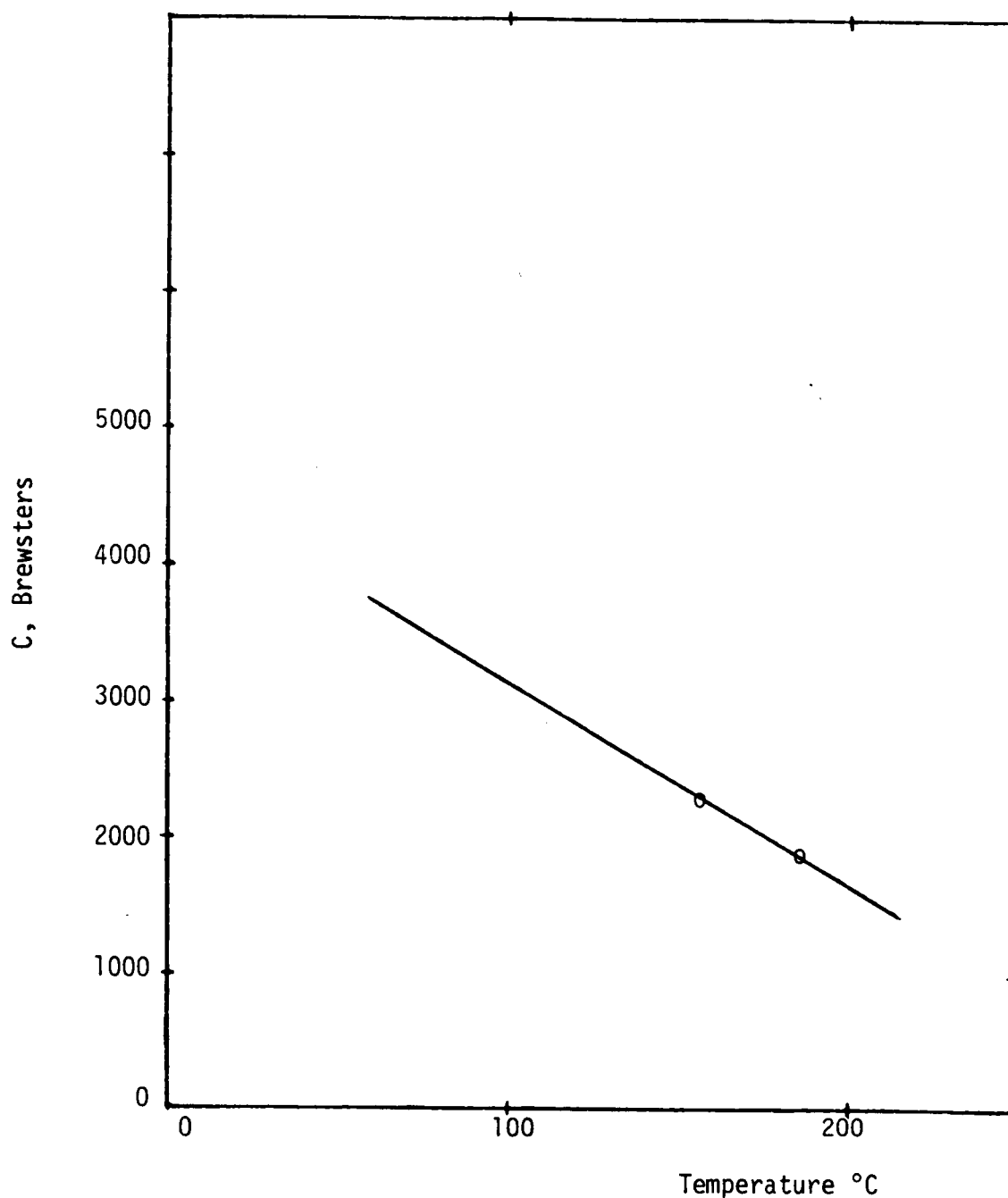


Figure A-7: Variation of Stress-Optical Coefficient of Polyethylene (HDPE) with Temperature.

Source: Wales, J. L. S. "The Application of Flow Birefringence to Rheological Studies of Polymer Melts," Delft Univ. Press (1976).

APPENDIX B

THERMAL STRESS ANALYSIS

Fourier heat conduction equation (with the viscous dissipation term neglected) is given by:

$$\rho C \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (kr \frac{\partial T}{\partial r}) \quad (B-1)$$

with boundary and initial conditions

$$T(r, 0) = T_0$$

$$\frac{\partial T}{\partial r}(0, t) = 0$$

$$-k \frac{\partial T}{\partial r}(a, t) = h[T(a, t) - T_s].$$

where k is the thermal conductivity, ρ is the density, C is the heat capacity, a is the filament radius, h is the heat transfer coefficient, T_s is the temperature of the surroundings, and T_0 is the initial melt temperature. The solution to this equation when k , ρ , C , and a may be considered constants is given by Carslaw and Jaeger (27) as:

$$\frac{T(r, t) - T_s}{T_0 - T_s} = \frac{2ah}{k} \sum_{n=1}^{\infty} \exp \frac{-\kappa \beta_n^2 t}{a^2} \frac{J_0(\beta_n \frac{r}{a})}{[\beta_n^2 + (\frac{ah}{k})^2] J_0(\beta_n)} \quad (B-2)$$

where $\kappa = \frac{k}{\rho C}$, and the β_n are the roots of the equation, $\beta J_1(\beta) - \frac{ah}{k} J_0(\beta) = 0$, J_0 and J_1 are Bessel functions of the first kind and zeroth and first order. In melt-spinning, the heat transfer coefficient h is represented by the expression due to Kase and Matsuo (62):

$$h = 0.21(1 + M)k_o \sqrt{\frac{\pi \rho V z}{W}} \left(\frac{2}{v_o}\right)^{0.334} \left(\frac{\rho W V z}{\pi}\right)^{0.117} \quad (\text{B-3})$$

where M is an adjustable parameter which depends on the direction of air flow with respect to the threadline, k_o is the thermal conductivity of ambient air, ρ is the density of the threadline being cooled (i.e., ρ varies with temperature), W is the mass flow rate, v_o is the kinematic viscosity of ambient air.

The roots β_n of the equation $\beta J_1(\beta) - \frac{ah}{k} J_0(\beta) = 0$ are such that $\beta_1 \ll \beta_2 \ll \dots \ll \beta_{n-1} \ll \beta_n$, and that only β_1 is of significant importance in Equation (B-2). According to Tsoi and Kianovskii (124), the first root β_1 is given approximately by

$$\beta_1^2 \approx \frac{6\left(\frac{ah}{k}\right)\left[4 + \frac{ah}{k}\right]}{\left(\frac{ah}{k}\right)^2 + 6\left(\frac{ah}{k}\right) + 12} \quad (\text{B-4})$$

where

$$\frac{ah}{k} < 0.1.$$

Thus, if all the other roots are neglected, Equation (B-2) reduces to:

$$\begin{aligned} \frac{T(r, t) - T_s}{T_o - T_s} &= \frac{2ah}{k} \left[\exp \frac{-\beta_1^2 t}{a^2} \frac{J_0\left(\beta_1 \frac{r}{a}\right)}{[\beta_1^2 + \left(\frac{ah}{k}\right)^2] J_0(\beta_1)} \right] \\ &= A \exp \frac{-\beta_1^2 t}{a^2} J_0\left(\beta_1 \frac{r}{a}\right) \end{aligned} \quad (\text{B-5})$$

where

$$A = \frac{2 \frac{ah}{k}}{[\beta_1^2 + (\frac{ah}{k})^2] J_0(\beta_1)} .$$

If t_{gc} is the time when the center temperature reaches T_g , then

$$\frac{T(0, t_{gc}) - T_s}{T_0 - T_s} = A \exp \frac{-\kappa \beta_1^2 t_{gc}}{a^2} . \quad (B-6)$$

The temperature distribution corresponding to t_{gc} is

$$\frac{T(r, t_{gc}) - T_s}{T_0 - T_s} = A \exp \frac{-\kappa \beta_1^2 t_{gc}}{a^2} J_0(\beta_1 \frac{r}{a}) . \quad (B-7)$$

Substituting (B-6) into (B-7) yields

$$T(r, t_{gc}) - T_s = (T_g - T_s) J_0(\beta_1 \frac{r}{a}) \quad (B-8)$$

Similarly, if t_g is the time when an outer shell of thickness $0.1a$ has solidified such that the temperature at $r = 0.9a$ is T_g , then the temperature distribution corresponding to t_g , will be

$$T(r, t_g) - T_s = (T_g - T_s) \frac{J_0(\beta_1 \frac{r}{a})}{J_0(0.9\beta_1)} . \quad (B-9)$$

Thermal stresses are essentially given as (27,54):

$$\frac{(1 - \nu)\sigma_{rr}}{E\alpha} = \frac{1}{a^2} \int_0^a T r dr - \frac{1}{r^2} \int_0^r T r dr \quad (B-10a)$$

$$\frac{(1 - \nu)\sigma_{\theta\theta}}{E\alpha} = \frac{1}{a^2} \int_0^a T r \, dr + \frac{1}{r^2} \int_0^r T r \, dr - T \quad (\text{B-10b})$$

$$\frac{(1 - \nu)\sigma_{zz}}{E\alpha} = \frac{2\nu}{a^2} \int_0^a T r \, dr - T \quad (\text{B-10c})$$

where

$$T = T(r, t) - T_s.$$

Equation (B-5) can be rewritten as

$$T(r, t) - T_s = (T_0 - T_s) \text{Aexp} \frac{-\kappa\beta_1^2 t}{a^2} J_0(\beta_1 \frac{r}{a}).$$

Substituting this in (B-10a), (B-10b), and (B-10c) and integrating yields:

$$\frac{(1 - \nu)\sigma_{rr}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [J_1(\beta_1) - \frac{a}{r} J_1(\beta_1 \frac{r}{a})] \text{Aexp} \frac{-\kappa\beta_1^2 t}{a^2} \quad (\text{B-11a})$$

$$\frac{(1 - \nu)\sigma_{\theta\theta}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [J_1(\beta_1) + \frac{a}{r} J_1(\beta_1 \frac{r}{a}) - \beta_1 J_0(\beta_1 \frac{r}{a})] \text{Aexp} \frac{-\kappa\beta_1^2 t}{a^2} \quad (\text{B-11b})$$

$$\frac{(1 - \nu)\sigma_{zz}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [2\nu J_1(\beta_1) - \beta_1 J_0(\beta_1 \frac{r}{a})] \text{Aexp} \frac{-\kappa\beta_1^2 t}{a^2}. \quad (\text{B-11c})$$

The average stress in the filament is computed using the expression

$$\sigma_{av} = \frac{1}{a} \int_0^a \sigma(r, t) dr.$$

Thus,

$$\frac{(1 - \nu)\sigma_{rr_{av}}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [2J_1(\beta_1) - \int_0^{\beta_1} J_0(x) dx] A \exp \frac{-\kappa\beta_1^2}{a^2} t \quad (B-12a)$$

$$\begin{aligned} \frac{(1 - \nu)\sigma_{\theta\theta_{av}}}{E\alpha(T_0 - T_s)} &= \frac{1}{\beta_1} [J_1(\beta_1) - J_1(\beta_1) + \int_0^{\beta_1} J_0(x) dx \\ &\quad - \int_0^{\beta_1} J_0(x) dx] A \exp \frac{-\kappa\beta_1^2}{a^2} t = 0 \end{aligned} \quad (B-12b)$$

$$\frac{(1 - \nu)\sigma_{zz_{av}}}{E\alpha(T_0 - T_s)} = \frac{1}{\beta_1} [2\nu J_1(\beta_1) - \int_0^{\beta_1} J_0(x) dx] A \exp \frac{-\kappa\beta_1^2}{a^2} t. \quad (B-12c)$$

To obtain the residual stresses, O'Rourke and Saenz (92) have suggested a model which leads to the following rule:

To calculate the residual stresses in a body A quenched from the uniform temperature T_1 to the temperature T_0 of a bath ($T_1 > T_0$), one calculates the thermal stresses at time $t = t^*$ ($T = T^*$) in an elastic body B, with the same elastic and thermal constants as A, whose initial temperature is T_0 and whose surface beginning at $t = 0$ is maintained

at T_1 . The stresses in B at $t = t^*$ are the negative of the residual stresses at $t \rightarrow \infty$ in A.

This rule can be applied in the present study by replacing t by t_{gc} and $t_{g'}$ in the stress equations and the negative of the resulting stresses will then be the required residual stresses.

$$\text{i.e., } \Delta^* = - \Delta \Big|_{t = t_{gc} \text{ or } t_{g'}}$$

where $*$ indicates residual stress.

The negative of the stress distribution obtained from cooling, and the residual stress distribution calculated based on the above model are plotted in Figures B-1 and B-2. The two methods yield nearly identical results, thus proving the validity of the methods.

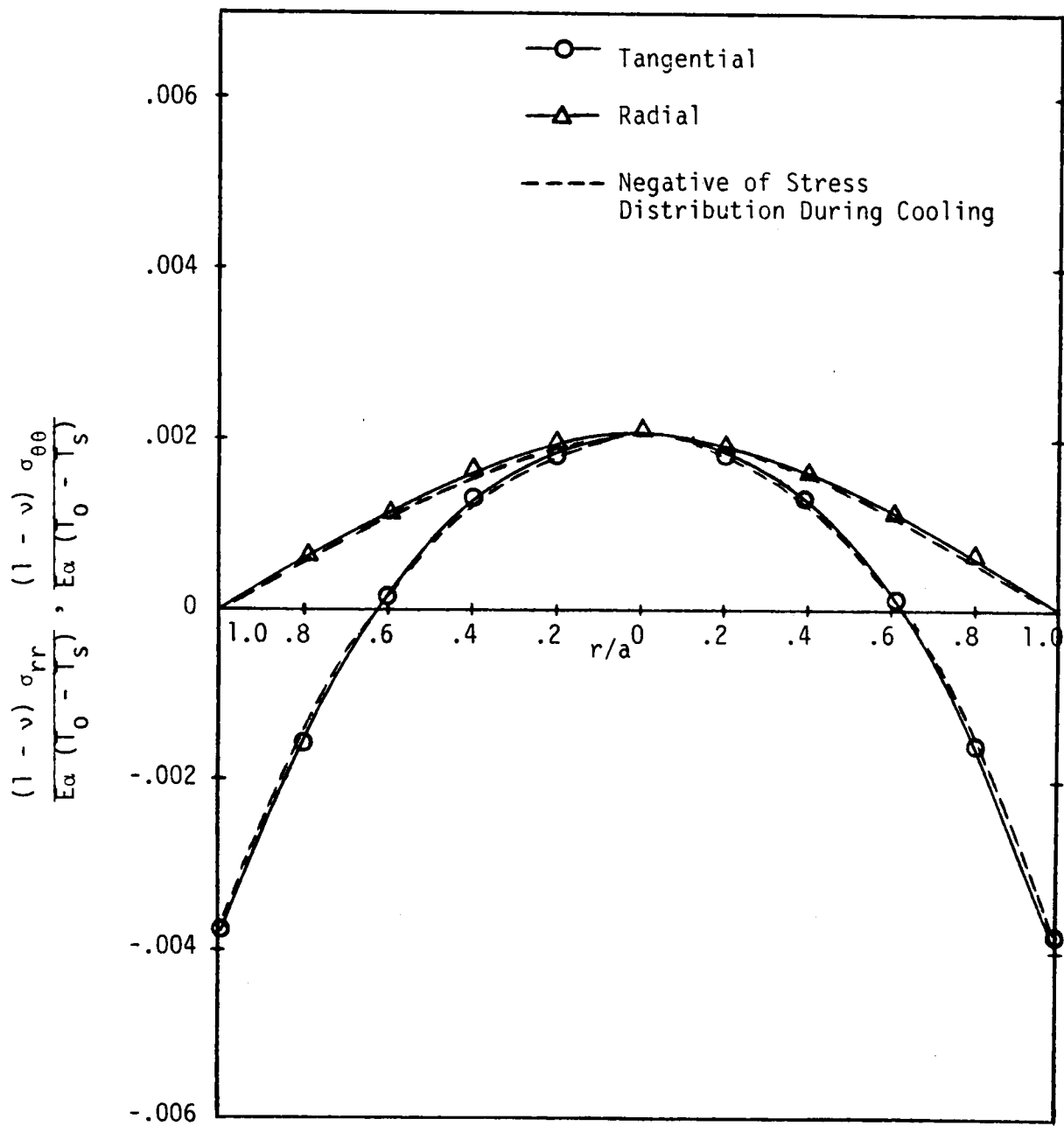


Figure B-1. The Dimensionless Radial and Tangential Stress Components of the Residual Stress from Cooling and Heating.

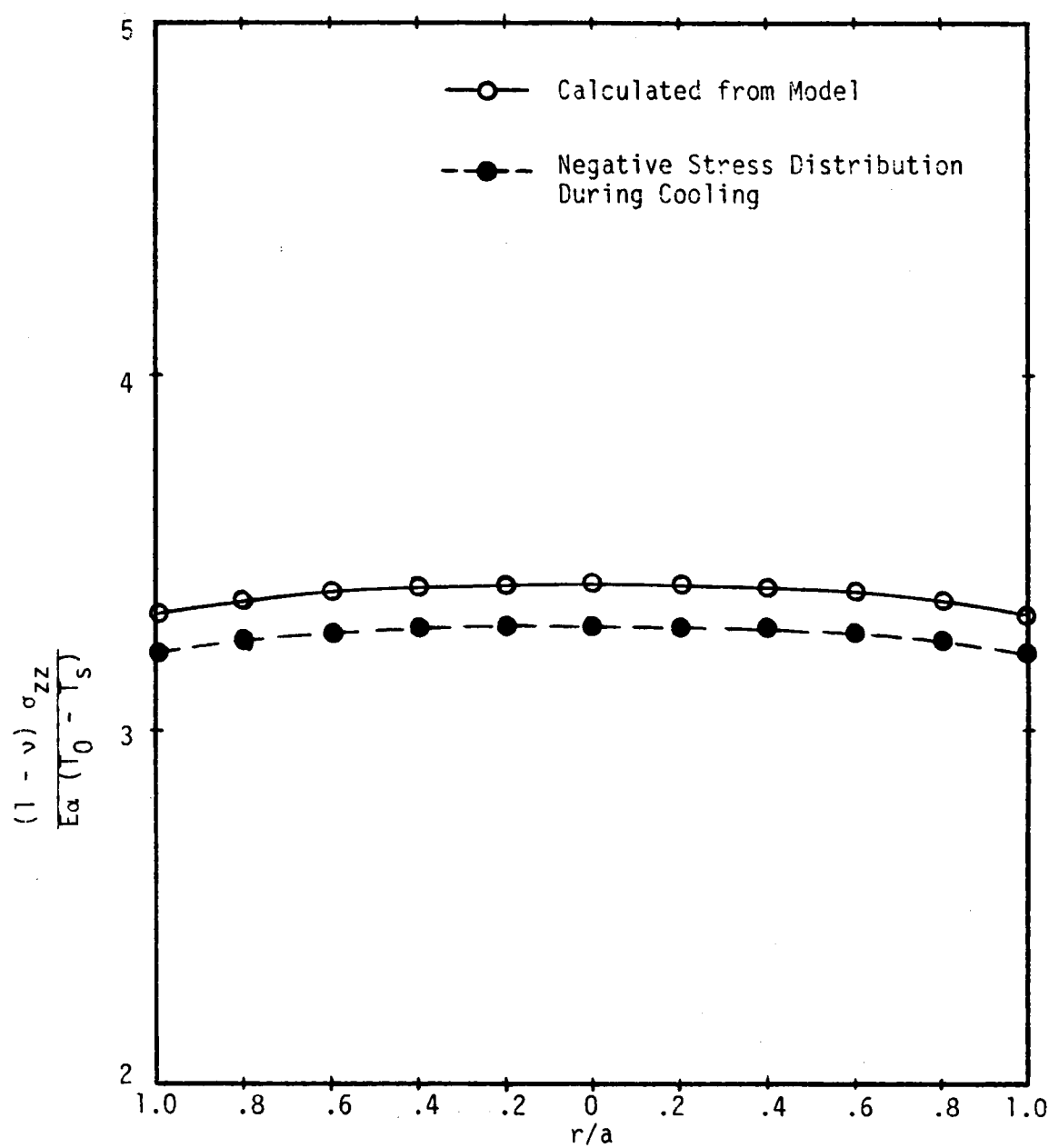


Figure 3-2. The Dimensionless Axial Stress Component of the Residual Stress from Cooling and Heating of PMMA.

VITA

Fredson Boateng, a native of Kumasi, Ghana, attended Opoku Ware Secondary School and the University of Science and Technology, both in Kumasi. He worked at Ashanti Goldfields Corporation, Obuasi, as a supervisory assistant in the Cyanidation Retreatment of Flotation Tailings section of the treatment plant. Next, he joined the teaching staff at Pope John's Secondary School, Koforidua, Ghana, where he taught physics and mathematics for two years.

He left Ghana for the United States in September 1972. He entered the University of California, Berkeley, and in August 1976, he received a Bachelor of Arts degree in Biological Sciences. Mr. Boateng then moved to Tennessee where he entered the Graduate School of The University of Tennessee, Knoxville, and was awarded the Master of Science degree in Polymer Engineering in June 1980.

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