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Robert M. Jennings

University of Massachusetts Amherst

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AN INVESTIGATION OF THE EFFECTS OF CURING CONDITIONS
ON THE RESIDUAL STRESS AND DIMENSIONAL
STABILITY IN POLYIMIDE FILMS

A Dissertation Presented
by
ROBERT M. JENNINGS

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1993

Polymer Science and Engineering Department
AN INVESTIGATION OF THE EFFECTS OF CURING CONDITIONS ON THE RESIDUAL STRESS AND DIMENSIONAL STABILITY IN POLYIMIDE FILMS

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ACKNOWLEDGMENTS

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four years. From Dr. Farris I have also learned quite possibly the most important
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financial support of this project.
ABSTRACT

AN INVESTIGATION OF THE EFFECTS OF CURING CONDITIONS ON THE RESIDUAL STRESS AND DIMENSIONAL STABILITY IN POLYIMIDE FILMS

FEBRUARY 1993

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A number of aspects on the processing of PMDA-ODA polyimides have been investigated. These aspects included the effects of curing procedure on residual stress development in polyimide films, characterization of stresses arising in films during processing on tenter frames and the effects of stress history on irreversible shrinkage behavior.

Chemical curing using a gel technique was found to reduce the development of residual stresses in PMDA-ODA films during cooling. Chemically cured polyimide films made from a gelation technique possessed consistently lower in-plane thermal expansion coefficients than thermally cured films. This was due to increased in-plane orientation development in the chemically cured films during drying.

An analysis of stresses arising during tenter frame processing of polymeric films indicates the presence of large in-plane shear stresses as a result of stress gradients along the machine direction. These shear stresses vary linearly across the width of the line and are responsible for creating orientational anisotropy and non-uniformity profiles across the width as well. The principal directions of stress tend to lie at ±45° to the
machine direction but may be altered by machine and transverse drawing by the frame. Methods to eliminate or at least reduce in-plane anisotropy were discussed as well.

An investigation of strain storage behavior revealed a strong relationship between irreversible shrinkage and stress history in several different polymeric materials. Irreversible shrinkage in polyimide films was found to be largely due to the cooling of the materials under stress. Shrinkage behavior in PMDA-ODA and Upilex-R® films could be described in a quantitative manner using linear viscoelasticity.

Two forms of highly crystalline PMDA-ODA based polyimide were formed by a high pressure imidization process. Polyimide powder with a density of 1.46±0.01g/cm³ was formed by curing a polyamic acid solution in dimethylacetamide at 200°C and 1.38 MPa. Heat treatment of chemically cured gel films under the same conditions resulted in films with a density of 1.44±0.01g/cm³.
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CHAPTER I

INTRODUCTION AND BACKGROUND

A. Introduction

1. Motivation

Residual stresses can have profound effects on the performance and lifetime of polymeric coatings. Many coating failures such as cracking and delamination, often attributed to material weaknesses, are actually a result of residual stresses caused by mechanical constraints imposed on the material. Usually, coatings are applied in a solution or melt state and must be dried and/or cooled to ambient conditions to form a solid film layer. During this process, the coating materials are often subjected to mechanical constraints in two and sometimes even three dimensions leading to the buildup of very large shrinkage stresses. Since residual stresses have a strong influence on failure mechanisms, it is usually important to find ways to minimize such stresses.

One technological field that has provided a great number of interesting problems for coating material engineers over the last decade has been microelectronics. In order to meet the ever increasing demand for speed and memory capacity in computers, electronics packagers have been forced to design modular systems with smaller components and finer tolerances. Many of the newer packaging schemes such as tape automated bonding (TAB) and multi-IC chip modules require large numbers of connecting leads with intimate contact between polymers and other materials. Concerns about polymeric material properties, such as dimensional stability, planarity and moisture resistance have become more important than in the past. Fine control over such properties requires an even greater understanding of the processing of high performance polymers.
Polyimides have emerged as a new class of insulating materials as dimensional and thermal requirements of electronic packaging materials have increased. Polyimides are often used in electronics applications as interlevel insulators, adhesives or flexible circuit board substrates. During the last decade, polyimides have also found their way into other uses such as magnetic recording substrates and high temperature composite applications. One reason for the popularity of these materials is their excellent thermal and chemical stability under very harsh environments. Most aromatic polyimides are strongly resistant to organic solvents and are chemically stable at temperatures up to 400°C. This allows them to be used under harsh conditions that exclude the use of most other organic materials. As a result, polyimides are often placed in abusive conditions where the unstressed material is chemically stable, but mechanical constraints can cause stresses large enough to cause coating failure.

Polyimides are also useful materials in the general study of coating stresses and dimensional stability for a number of reasons. The understanding of polyimide stresses has a direct impact on many electronic packaging technologies. Polyimides are also a relatively well behaved material from a mechanical perspective. Most commercial aromatic polyimide films do not exhibit appreciable crystallinity and often have glass transition temperatures ($T_g$) greater than 300°C, thus providing reasonably constant thermal and mechanical properties over a wide range in temperature.

Although there are several different types of high temperature aromatic polyimides available, this study will focus primarily on poly-[N,N' bis-phenoxyphenyl pyromellitimide] or PMDA-ODA in reference to its monomeric constituents. This material is one of the more commonly used polyimides known more often by its commercial name, Kapton®, produced by duPont. PMDA-ODA is a tough, glassy material with a room temperature modulus around 3 GPa, an ultimate failure strength of about 250 MPa and an estimated $T_g$ of 400°C. Although PMDA-ODA can be swollen...
by a few solvents including water, it is insoluble to all known non-acidic organic solvents and is chemically stable in air at temperatures up to 450°C for brief periods of time.

Since PMDA-ODA has no melting transition and is only soluble in very strong acids (which also degrade the polymer), its precursor, polyamic acid, is processed in solvents such as N-methyl-2-pyrolidinone (NMP), dimethyl formamide (DMF) or dimethyl acetamide (DMAc). Polyimide films can be produced by simply coating the precursor solution onto a substrate then baking the material to remove solvent and allow imidization to take place. Commercial polyimide films are produced on tenter frames with the aid of a chemical cure method as shown in figure 1.1. Typically, curing temperatures must exceed 300 to 400°C to achieve optimum mechanical properties.

During the process of curing, both orientation and stresses develop in the material. Orientation is known to have a large influence on the modulus and thermal expansion behavior of the material. This in turn effects stress development during the final cooling stages of cure. It must be noted that not all the curing stresses reveal themselves upon cooling. Some stresses become frozen into the material as stored strain energy during cure and manifest themselves as non-reversible shrinkages upon later heating. Although this type of behavior is sometimes common in polymers and even useful in many packaging applications, it can be detrimental in many applications of these materials.

2. **Dissertation Overview**

The overall objective of this work is to further understand and control curing stress development in polyimide coatings. This project will focus on two main aspects of stress development during cure. The first part will attempt to determine how curing conditions and processing history contribute to the stress behavior in these materials in both coating and commercial processing. This will be accomplished using a combination of modeling
Cooling
Mixing / Coating
Thermal Treatment
Oven
Cooling

(Figure 1.1) Schematic of tenter frame processing line.
and experimental techniques. The second part of this project will focus on understanding how stresses become frozen into the material during cure. An attempt to account for the stored strain energy will be made by following the stress and strain behavior in the material during various stress and thermal histories.

The results of this work are divided into four main areas. The curing methods and stress measurement techniques used in this study will be shown in Chapter II. A discussion of effects of orientation and thermal expansion behavior in polyimides will also be included in Chapter II. Chapter III will focus on strain storage and irreversible shrinkage in non-crystallizing materials. An analysis of the stresses arising during tenter frame processing will be presented in Chapter IV along with the consequences of these stresses on orientation and shrinkage behavior in the final product. Chapter V contains a preliminary characterization of novel forms of highly crystalline PMDA-ODA based polyimide and Chapter VI will provide a summary of the entire thesis research along with some general conclusions.

B. Background

1. Literature Review of Polyimides

The review of polyimide literature of interest to this study will be divided into three categories: chemistry, physical properties and stress development.

a. Chemistry

The first polyimides were made from amide salts\cite{8,9,10}. These salts were formed from aromatic tetra-functional acids and aliphatic diamines and when heated produced a polyimide melt that could be extruded or injection molded at temperatures between 300
and 400°C. In a search for higher temperature insulating materials, a two-step synthesis for the preparation of wholly aromatic polyimides was developed by duPont in the late 50's and early 60's. In this process, a dianhydride is reacted with an aromatic diamine at low temperatures in solution to form a polyamic acid precursor (figure 1.2). This polymer is soluble in solvents such as NMP, DMF, DMSO, or DMAc that allows film formation in the precursor solution state.

The polyamic acid may be converted to the polyimide by a cyclizing dehydration reaction which takes place generally between 150 and 200°C or by treating the polyamic acid with anhydride and amine curing agents that allow imidization to start at room temperature (figure 1.3). In both cases reaction is essentially complete below 200°C with a yield somewhere between 50 and 85%. However, the material is usually thermally treated at temperatures above 300 to 400°C to take advantage of ordering effects which occur at these temperatures and to impart mechanical stability to the films over a wider range of temperatures.

Endry (1965) cited a number of different anhydride and amine combinations that may be used to induce imidization. The activity of the amine was reported to have an effect on the extent of conversion. Highly active amines such as trimethyl amine and triethylene diamine were reported to induce a more efficient conversion than less active amines such as 2,6-lutidine and 2,4,6-colidine. Amines such as pyridine and 3-methylpyridine (3-picoline) were reported to be the most effective curing agents. Vinogradova (1974) reported that the basicity of the amine had a strong effect on the yield and molecular weight of 3,3',4,4'-benzophenone dianhydride, 9,9-bis(4-aminophenyl) fluorene polyimides. In most cases, conversion using highly basic amines (pKₐ ≥ 10) such as trialkylamines resulted in higher yields and higher molecular weights than less basic amines (pKₐ 4-7). Pyridine, 2-methylpyridine and isoquinoline proved to be exceptions (pKₐ 5.2-5.7).
pyromellitic dianhydride + \[H_2N-\text{bis(4-aminophenyl)ether} \quad (4,4'\text{-oxydianiline})\] 

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(Figure 1.2) Polyamic acid synthesis
(Figure 1.3) Reaction schemes for curing polyamic acid to polyimide. 

Thermal Cure Route

Chemical Cure Route
There has been some debate in the literature over whether polyamic acids covalently crosslink during cure. The primary arguments supporting this idea suggest that crosslinking could take place by a competing intermolecular dehydration reaction that would produce amide linkages between imide main chains\textsuperscript{19,20}. Opponents to this argument point out the unlikelihood of distant nucleophiles from neighboring chains competing with nucleophiles along the same chain for attack on active amic-acid groups\textsuperscript{21}. Light scattering measurements performed by Volksen and Cotts (1987) on polyamic acids in NMP and their corresponding polyimides dissolved in concentrated sulfuric acid, revealed a slight decrease in molecular weight during thermal cure attributed to either random error or slight degradation during reaction. It has been suggested that the strong agreement between molecular weight measurements on polyamic acids and polyimides indicates that side reactions that would change the molecular weight distribution, such as crosslinking and degradation, provide little contribution during the imidization reaction\textsuperscript{21,22,23}. Snyder et al. (1989) point out that the slight decrease in molecular weight during cure could be significant and that intermolecular amide linkages would be expected to be more susceptible to cleavage in strong acids causing a decrease in molecular weight\textsuperscript{20}.

Infrared studies performed on monomeric model compounds suggest side products such as isoimides and possibly even intermolecular links are probably formed at least to some small extent during imidization. The studies also suggest that the side reactions are more likely to occur during chemically assisted imidization reactions\textsuperscript{19,20}. Although isoimide groups have been found using infrared spectroscopy in chemically cured PMDA-ODA prior to heating, they quickly isomerize to form imides at higher temperatures\textsuperscript{12,14}. Infrared measurements performed by Pryde (1989) revealed little evidence of intermolecular linkages formed in thermally cured films leading to the conclusion that if intramolecular linkages are formed during thermal curing they are in concentrations too low to be readily identified by infrared spectroscopy\textsuperscript{24}. Another
recent study by Jou and Huang (1991) reported substantial formation of intermolecular linkages in polyimides based on pyromellitic dianhydride and p-phenylenediamine (PMDA-PDA). However, conclusive evidence of covalent crosslinking in PMDA-ODA could not be found.

b. Physical Properties

Mechanical properties such as the tensile strength and the elongation at break for PMDA-ODA have been shown to vary sigmoidally with the molecular weight of the precursor polyamic acid. These properties generally achieve optimum limiting values for weight-average molecular weights greater than 30,000 to 40,000 corresponding to a degree of polymerization (DP) of 75-100 for PMDA-ODA. This is lower than generally found for most linear polymers. Polymers such as polyamides and polyesters exhibit property limiting DPs at greater than 200 while aliphatic polymers generally need DPs greater than 500. The low critical degree of polymerization for polyimides is often found in linear polymers with strong intermolecular bonding capacity. Kevlar® (poly-[p-phenylene terephthalamide]), which is known to have strong intermolecular interactions, shows a property limiting DP in the range of 100 repeat units. Modulus and thermal expansion, which are not as affected by these interactions, do not show a strong dependence on molecular weight, for weight-average molecular weights greater than 8000.

Polyimides are known to be highly susceptible to intramolecular interactions. It has been shown that polyamic acid can form complexes with NMP and other solvents through hydrogen bonding and that these bonds do not break down at temperatures less than 150°C thus inhibiting imidization from taking place below this temperature. It has also been suggested that these polymer-solvent interactions are strong enough to facilitate side reactions of the polyamic acid with solvent causing some degradation.
during cure. Feger showed by dynamic mechanical studies on partially cured PMDA-ODA that as solvent decomplexes it plasticizes the polymer and allows imidization to proceed. As conversion continues, the glass transition of the partially cured polyimide increases until it reaches the current cure temperature. This decreased mobility in the system inhibits further reaction and solvent removal from taking place. Once the new T_g of the system is surpassed, reaction and solvent removal continue until the T_g increases above the current cure temperature again. Palmese et al. (1987) demonstrated using time-temperature-transformation (TTT) diagrams that the T_g's for polyamic acid / polyimide systems are closely tied to the cure temperature.

The high T_g's of pyromellitimide based polyimides have been presumed to be a result of strong intermolecular interactions in the solid state of these materials. Polymer-polymer interactions have also been blamed for the sensitivity of viscosity measurements on concentrated polyamic acid solutions to effects other than molecular weight. A few different models have been proposed to account for polymer-polymer interactions. Kotov et al. (1977) proposed the presence of a charge-transfer complex (CTC) between dianhydride and diamine groups in the main chains based on UV spectroscopy studies. Fryd (1984) suggested that this charge-transfer complex increases interchain interaction forces thus increasing the T_g's of these materials. Other authors have proposed that the high T_g's of pyromellitimides is due to a layered packing of diimides in polyimides.

X-ray scattering studies performed on PMDA-ODA films cured to different temperatures reveal the appearance of a sharp reflection at 16 Å and a halo at 5 Å for curing temperatures between 280 and 300°C that increase in sharpness with higher curing temperatures. These reflections are attributed to a smectic-like order phase that develops from the initial phase aggregation in the polyamic acid. Isoda (1981) reported that the degree of ordering is closely tied to the initial cure temperature and that later curing to higher temperatures had little effect on the initial structure.
created in the material\textsuperscript{37}. Three different unit cells have been proposed for PMDA-ODA\textsuperscript{36,41,42}. Although all three suggest that the order regions consist of face-centered, laterally packed chains in a 2\textsuperscript{1} helical conformation, they disagree on the shape and dimensions of the unit cell. Two studies based on WAXD measurements on oriented PMDA-ODA fibers and semi-empirical quantum chemical calculations suggest an orthorhombic unit cell\textsuperscript{41,42} while one study based on X-ray measurements on oriented Kapton\textsuperscript{®} H film and Van der Waals' energy calculations suggest a monoclinic unit cell with $\beta=100^\circ$\textsuperscript{36}. Small angle X-ray scattering (SAXS) studies performed on PMDA-ODA films indicate the presence of voids with sizes ranging from 50 to 150 Å. However, it was also demonstrated that the fraction of these voids was only 0.07\% of the total material volume\textsuperscript{43}.

Numata et al. (1987) demonstrated that constraints imposed on films during cure have little effect on the density of many aromatic polyimide films and proposed that constraints should have little effect on the degree of aggregation as well\textsuperscript{44}. However, constraints imposed on films during cure did have a profound effect on the in-plane thermal expansion coefficients of the films. Thermal expansion coefficients measured on constrained films were an average of two to three times lower than coefficients measured on unconstrained films. The lower thermal expansion coefficients and higher moduli in constrained films were attributed to increased in-plane orientation developed during cure. Other studies demonstrate a strong correlation between molecular chain stiffness and the modulus and thermal expansion behavior of polyimides\textsuperscript{45,46,47}.

Planar orientation in PMDA-ODA films has been observed using both SAXS and birefringence measurements\textsuperscript{38,48,49}. Ikeda (1966) first noticed a preferred alignment of polymer chains parallel to the surface in PMDA-ODA films using X-ray diffraction\textsuperscript{35}. WAXD measurements made later by Russell (1983) gave an estimated crystalline orientation out-of-plane function of about -0.20 for thermally and -0.24 for chemically cured polyimide films\textsuperscript{48}. Waveguide birefringence measurements on thermally cured
films also show that the out-of-plane birefringence (i.e. the difference between the refractive index through the thickness and the average in the plane) closely follows the thickness changes in the film due to solvent loss increasing rapidly with temperature between 79°C and 215°C. Several studies have reported an out-of-plane birefringence of -0.08 for PMDA-ODA thermally cured on glass and Pyrex substrates. It also was demonstrated that cure temperatures above 215°C have little effect on orientation.

Several authors have noted in-plane anisotropic behavior in commercial polyimide films. Argon and Bessonov (1977) reported noticeable birefringence in Kapton® film. Blumentritt (1978) reported significant in-plane anisotropy in the modulus, ultimate strength, thermal expansion, and hygroscopic expansion in Kapton® with the largest difference in properties occurring ±45° to the machine direction. These studies also showed a significant amount of non-uniform irreversible shrinkage in Kapton. Beohme and Cargill (1984), using X-ray scattering measurements on Kapton® films, determined that there is a preferential in-plane alignment of polymer chains approximately 60±15° to the machine direction. Sackinger and Farris (1990) also found in-plane anisotropic behavior in modulus and thermal expansion in both Kapton® and Upilex® (ICI) films. This anisotropy has been attributed to stress profiles developed during line processing.

c. **Stresses in Polyimides**

It has been demonstrated from in-situ measurements that stress development during curing of polyimides arise from essentially two sources: solvent removal and cooling. Bauer and Farris (1988, 1989) showed that in the early stages of thermal curing the drying stresses dominate and can be as large as 10 to 12 MPa in uniaxially constrained polyamic acid. Sackinger and Farris (1990) later showed that swelling of fully cured polyimides by various solvents can cause stress changes of as much as 40 to 50 MPa in uniaxially constrained films.
Although drying stresses dominate during the initial stages of cure it has been shown that the final state of stress in polyimides results from cooling stresses\textsuperscript{59,60}. In some of the early work on measuring curing stresses in polyimides, Goldsmith et al. (1983) demonstrated that stresses in an aromatic polyimide based on a modified benzophenone-tetracarboxylic acid (BTDA) and methylene dianiline (MDA) are a result of cooling from the cure temperature and that the final stress in the material is a function of the curing temperature\textsuperscript{59}. Biaxial curing stresses as high as 75 MPa were reported for films cured at 400°C using a beam bending stress measurement technique. Elsner (1987) demonstrated using a modified beam bending technique that the final biaxial stresses in PMDA-ODA vary almost linearly with the highest cure temperature used for cure temperatures above 200°C\textsuperscript{60}. Biaxial stresses as high as 65 MPa were reported for films cured at 400°C.

2. **Stresses in Coatings**

Coating stresses develop as a result of mismatch in dimensional changes between the coating and substrate materials. These dimensional changes can be caused by changes in environment such as temperatures and humidity or by changes in the coating material, such as chemical reaction or crystallization. In many cases, the behavior of the coating materials during these processes can be represented using approximations based on linear elasticity. The constitutive equation for a linear, elastic, homogeneous, isotropic material whose properties can change with time, temperature and other environmental condition can often be expressed in an incremental form:

\[
(1 + v)d\sigma_{ij} - v\delta_{ij}d\sigma_{kk} = E [d\varepsilon_{ij} + \delta_{ij}(\alpha dT + \beta dc + \xi dx)]
\]

(1.1)

where

\[ E = \text{tensile modulus} \]
\( v = \text{Poisson's ratio} \)
\( \alpha = \text{linear thermal expansion coefficient} \)
\( \beta = \text{linear swelling expansion coefficient} \)
\( \xi = \text{linear reaction expansion coefficient} \)
\( T = \text{temperature} \)
\( c = \text{solvent content} \)
\( x = \text{degree or reaction} \)
\( \varepsilon_{ij} = \text{strain} \)
\( \sigma_{ij} = \text{stress} \)
\( \delta_{ij} = \text{Kronecker delta}. \)

Incremental elasticity theory makes the assumption that non-linear material properties, such as modulus and thermal expansion, can be treated as constant over an incremental change in environmental conditions. Although material properties are constant within each increment, the properties may change from increment to increment. The overall response of a material can be obtained by summing over all of the individual increments that comprise a process.

It has been demonstrated that interfacial shear stresses only become important at the edges of coatings\(^{61}\). Within a distance of about 5 to 7 thicknesses from the edge of a coating, these interfacial shear stresses disappear giving a state of stress that is essentially independent of the presence of an underlying substrate. As a result, the general state of stress in any two-dimensionally constrained system can be effectively described by a two-dimensional version of equation 1.1:

\[
\begin{align*}
\text{d}\sigma_{xx} &= \frac{E}{(1 - v^2)(d\varepsilon_{xx} + v d\varepsilon_{yy})} - \frac{\alpha E dT}{(1 - v)} \\
\text{d}\sigma_{yy} &= \frac{E}{(1 - v^2)(d\varepsilon_{yy} + v d\varepsilon_{xx})} - \frac{\alpha E dT}{(1 - v)} \\
\text{d}\sigma_{xy} &= \frac{E}{(1 + v) d\varepsilon_{xy}}
\end{align*}
\]  

(1.2)
where $\sigma_{xx}$ and $\sigma_{yy}$ denote the in-plane normal stresses and $\sigma_{xy}$ represents an in-plane shear stress. The strains are defined in a similar manner. Note that only thermal effects are considered in the relation above. Swelling and other features can be described in a similar manner. The major consequence of the absence of interfacial shear stresses is that films processed on frames, such as in tenter frame processing, can potentially have the same stress states as films processed on substrates.

If the state of stress in the coating is isotropic and the source of dimensional constraint on the coating is a rigid underlying substrate, then equation 1.2 reduces further to:

$$d\sigma_{xx} = d\sigma_{yy} = \frac{-(\alpha_c - \alpha_s)E}{(1 - v)}dT$$ (1.3)

where $\alpha_c$ and $\alpha_s$ are the thermal expansion coefficients of the coating and substrate materials. As a result, the stress in a coating is dictated by the stiffness of the coating and the difference in thermal expansion coefficients between the coating and substrate materials.

3. **Stress Measurement Techniques**

A number of techniques currently exist for the measurement of residual stresses in polymeric coatings. The most widely used and accepted technique has been beam bending\textsuperscript{59,60,62}. In this technique, a coating is applied to a thin but rigid substrate material and cured. As stress develops in the coating, the substrate bends slightly. With knowledge of the substrate modulus and measurements of the substrate curvature the coating stress can be obtained in a very straightforward manner. Since the beam deflections are typically very small (on the order of the coating thickness), several
variations of this technique have been proposed using different optical techniques to measure the curvature.

Maden and Farris (1990) presented a vibrational technique where stresses are found by determining the resonant frequencies and modes of vibration of free standing, constrained membranes$^{63,64}$. The frequencies and modes of vibration are found using a time-averaged holographic apparatus. A few different techniques were described for removing a coating from a substrate while still preserving the state of stress in the coating material. Other techniques exist using similar samples where the coating stresses can be found by placing a small pressure gradient across the drum-like and measuring the resulting deflection profile or by pushing a probe into the center of the membrane and measuring the resulting load and deflection$^{65}$.

All the techniques describe above can be used to obtain reliable stress measurements when used properly. However, each technique has its own advantages and disadvantages. The beam bending techniques, while being fairly easy to perform, often require very sensitive techniques to measure the resulting deflections and are only usable for measuring isotropic stresses. The holographic technique has the advantage of providing both the principal stress and directions for coatings under anisotropic stresses$^{64}$. However, the apparatus required is relatively more involved and requires numerical corrections when used in environments other than vacuum. The membrane deflection techniques have the advantage of being very simple and easy to perform under most environments. However, the techniques currently encounter problems when used on rigid samples$^{65}$. It should be noted that in many cases where only isotropic coating stresses are desired and sufficient information is known about the Poison's ratio of the coating, a simple one-dimensional stress measurement can suffice using a good thermal mechanical analyzer with a constant strain option.
References


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CHAPTER II
CURING EFFECTS

A. Introduction

Polyimide films undergo several physical and chemical changes during the course of cure including solvent removal, imidization, orientation and to a small extent, crystallization. These changes in turn effect stress and property development in these materials. Although much attention has been given to the effects of thermal curing on residual stress and structural development, most studies on the chemical curing of polyimides have centered on changes in the molecular features such as molecular weight, isoimide formation and the possibility of covalent crosslinking. Investigations in this study will look at different curing techniques and their effects on the development of mechanical properties and stresses in polyimide films.

It has been demonstrated that the two processes which most affect stress development during the curing of polyimide films are solvent removal and cooling. During thermal curing, a polyamic acid solution is coated onto a substrate then subjected to a number of thermal treatments. Initially the coating is a liquid and does not support stress development until vitrification occurs. Bauer and Farris investigated stress and modulus development during solvent removal using impulse viscoelastic and time-of-flight techniques. These studies demonstrated that significant stresses did not develop in polyamic acid coatings until they were heated to 85°C when a large portion of the solvent had evaporated. In the dried state, polyamic acids demonstrated moduli similar to those of fully cured polyimide films.

In contrast, it will be demonstrated that during chemical curing, as used in the manufacture of many commercial polyimides, films are capable of supporting stresses at
lower polymer concentrations. Measurements of stresses during chemical and thermal curing were performed using holographic interferometry and membrane deflection techniques. These stresses will be related to measurements of orientation, thermal and mechanical properties to assess the effects of imidization and solvent removal on stress and property development in polyimides.

B. Experimental Methods

1. Description of Curing Techniques

Polyamic acid coatings were made from a 15 wt% stock solution of poly-[N, N' bis-phenoxynphenyl pyromellitamic acid] in dimethylacetamide (DMAc) obtained from duPont. The weight average molecular weight of the polymer was approximately 74000 g/mol. Solid polyamic acid films were made by either spin or blade coating the stock solution onto glass slides then drying under vacuum at room temperature. Observations with an Olympus® optical microscope under cross polarizers revealed no preferential in-plane orientation in fully cured films made as a result of either coating technique.

Thermal curing of polyamic acid coatings was performed in two stages. In the first stage, the coatings were placed on a hot plate at ~100°C for 1 hour to remove the majority of the solvent. The samples were then placed in a vacuum oven for 1 hour to complete the second stage of cure. Oven temperatures varied from sample to sample. However, most cures were performed at either 300°C or 400°C.

Unconstrained polyimide films were made by coating the polyamic acid solution onto a glass substrate treated with a Teflon® spray. The films were gently peeled off the substrate just after vitrification then thermally cured on a Teflon® film. During thermal
treatment the polyamic acid films shrank to about 50 to 60% of their original in-plane dimensions and increased in thickness.

Chemical curing was performed by two different methods. Chemical bath cured films were made by placing fresh polyamic acid coatings into a bath of 1:2:24 molar ratio of acetic anhydride, 3-picoline and cyclohexane for 30 minutes. All solvents were obtained from the Aldrich® Chemical Company and were used without further purification. Although pyridine is typically used as the amine component, 3-picoline was used in this study due to its lower volatility and its equivalent results in curing. Films were then dried at room temperature overnight.

Acetic anhydride and 3-picoline solutions were prepared in DMAc with concentrations of 7.2 mol/L. Chemical gel films were made by mixing stoichiometric amounts of the acetic anhydride and 3-picoline solutions directly into the polyamic acid solution prior to coating. One ml of each curing solution was added to the 15 wt% polyamic acid solution and mixed rapidly with a stirring motor. The mixture was then placed in a centrifuge for 1 minute to eliminate air bubbles then either blade or spun coated onto a glass substrate. After ~5 minutes at room temperature, the liquid coating formed an elastic gel that was dried at room temperature. Chemically cured films must go through an additional thermal cure as described above in order to produce fully cured films. Although thicknesses varied during cure, the thicknesses of all thermally treated films ranged between 13 and 18 μm.

2. Stress Measurement Techniques

In-situ uniaxial stress measurements were made using a force-temperature/swelling apparatus shown in figure 2.1. Sample ribbons with dimensions 8.0 by 0.5 cm were made from polyamic acid and chemically cured samples and cured in the apparatus. Samples are held at constant length and subjected to various environments
(Figure 2.1) Diagram of force-temperature/swelling apparatus.
including temperature changes up to 450°C. The environmental chamber is also capable of being flooded with various solvents. Loads were measured using an Interface 10 lb load cell and initial strains were imposed on samples using a scissor jack.

Biaxial stress measurements were made using both time-average holographic interferometry and membrane deflection techniques shown in figures 2.2 and 2.3. The principles behind the techniques and sample preparation have been discussed at length in previous publications by Maden and Farris\textsuperscript{22} and by Jennings, Taylor and Farris\textsuperscript{23}. Samples for both techniques were produced by making coatings on tin-coated steel substrates. The tin layer was approximately 175 μm thick. Steel washers (40mm ID, 60mm OD) were then adhered to the polymer coating using epoxy and the entire assemblies were placed in a bath of mercury. Over the course of about an hour the mercury amalgamates the tin producing drum-like membranes with the preserved coating stresses.

Polymer coatings on tin coated steel substrates were limited to thermal treatments less than 220°C due to the low melting point on the tin interlayer (231.9°C). Samples mounted on steel washers were capable of being thermally treated at higher temperatures by clamping the washer to a second washer to make a steel-polyimide-steel sandwich assembly. The clamped samples could undergo a proper thermal treatment with no slippage occurring.

Stresses from holography are found by determining the resonant modes and frequencies of vibration of the samples under vacuum. The isotropic residual stresses are related to the resonant frequencies through the following relation:

$$\sigma = 4\pi^2 \frac{R^2 f_{i,n}^2}{Z_{i,n}^2}$$

where

- \(f_{i,n}\) = frequency of vibration
- \(R\) = sample radius
- \(Z_{i,n}\) = nth zero of the \(l\)th order Bessel Function
(Figure 2.2) Diagram of holographic interferometry apparatus.
(Figure 2.3) Diagram of membrane deflection apparatus.
\[ \rho = \text{sample mass density} \]
\[ \sigma = \text{residual stress}. \]

Stresses from membrane deflection are found by pushing a flat 4 mm diameter circular probe into the center of the sample and measuring the slope of the resulting force verses deflection curve. The stress is related to the slope through the following relation:

\[ \sigma = \frac{F}{2\pi tu_a} \ln(a/b) \]  \hspace{1cm} (2.2)

where
\[ a = \text{probe radius} \]
\[ b = \text{sample radius} \]
\[ F = \text{measured force} \]
\[ t = \text{sample thickness} \]
\[ u_a = \text{probe deflection} \]
\[ \sigma = \text{residual stress}. \]

Stress measurements from the membrane deflection technique have been found to correlate very well with measurements made using holography for samples with thicknesses less than 50 \( \mu \text{m} \). Membrane deflection measurements were made on a Dynastat\textsuperscript{®} dynamic mechanical tester specially fitted with a 450 g load cell and interfaced with a personal computer. Both holography and membrane deflection provide measurements of residual stress without any prior knowledge of material mechanical properties.

3. **Measurement of Material Properties**

   a. **Mechanical Properties**

   Tensile moduli were measured using an Instron\textsuperscript{®} Universal Tensile Tester. Tests were performed on 8.0 by 0.5 cm ribbons at a draw rate of about 10\%/min. The ribbons
were bonded to cardboard tabs with epoxy to prevent grip slippage. The machine compliance of this apparatus was negligible for the samples tested.

b. Densities

Densities were measured by a floatation technique. Films were submerged in a miscible mixture of carbon tetrachloride and p-xylene inside a 50 ml graduated cylinder. Various amounts of either solvent were added until films became buoyant in the solution. The density of the solvent mixture was then carefully determined by weighing 10 ml quantities at 25°C.

c. Thermal Expansion

Thermal expansion coefficients (TEC's) were measured using a TA Instruments® 2940 thermal mechanical analyzer (TMA) with a film and fiber attachment. All samples were first heated to 450°C in the TMA before measurements were taken to ensure reversible TEC measurements on heating and cooling. All heating and cooling cycles were performed at 5°C/min and TEC's verses temperature were determined by calculating linear regression slopes of the strain data over a ±10°C range.

4. Orientation Measurements

Out-of-plane birefringence measurements were performed using a reflection technique show in figure 2.4. Polyimide coatings were made on front silvered, mirrored glass substrates and cured using the techniques described earlier. A plane polarized He-Ne laser (\(\lambda = 6328\text{Å}\)) oriented at +45° was reflected off the sample at an angle of 45°. The retardation of the reflected beam was measured using a Babinet compensator and related to the out-of-plane birefringence using a modification of the relation derived by Stein for tilting birefringence measurements\(^{24}\):
(Figure 2.4) Optical setup for out-of-plane birefringence measurements on liquid and solid coatings.
\[ n_\perp - n_\parallel = \frac{\lambda}{2t} \left( R_0 - R_\phi \sqrt{1 - \frac{(\sin^2 \theta)/n^2}{(\sin^2 \theta)/n^2}} \right) \]  

(2.3)

where

\( \lambda \) = wavelength of light  
\( \theta \) = angle of incidence  
\( n_\perp, n_\parallel \) = refractive indices perpendicular and parallel to film surface  
\( n \) = average refractive index  
\( R_0 \) = in-plane retardation  
\( R_\phi \) = measured retardation  
\( t \) = film thickness.

The film thicknesses during cure were estimated by measuring the mass of the coatings during and after cure, measuring the thickness of the final dried film, and assuming volume additivity of the solvent and polymer.

In order to account for the effects of internal reflection on the measured retardation, calculations based on the Fresnel equations were performed for light reflecting off a polyimide coating at 45° to the surface normal. For these calculations, shown in Appendix A, absorption of light by the materials was ignored. It was estimated that about 58% of the measured beam intensity comes from light reflected only once off the substrate surface with the balance of the signal coming from light reflected off the upper coating surface and higher order reflections within the coating. It was found that for film thicknesses between 20 and 200 μm and for birefringences ranging between -0.02 and -0.20, internal reflection induces an error of only about 10-20% in retardation measurements.
C. Experimental Results

1. Stress Development

The study of stress development in polyimide films was broken into two parts. During the first part, the effect of different curing techniques on thermal stress development was studied. Stress development prior to thermal treatment was then studied in the second part.

a. Thermal Curing

Biaxial stresses of polyimide films before and after thermal treatment were made using holographic interferometry and membrane deflection. All thermally treated samples were cured at 300°C under vacuum and the results of the measurements on thermally and chemically cured polyimides are shown in table 2.1. Although films made using the gel technique resulted in much higher stresses after solvent removal, these films produced the lowest residual stresses after thermal treatment. Films made by the chemical bath technique resulted in higher stresses than dried polyamic acid films but resulted in almost identical residual stresses to thermally cured films after thermal treatment.

In order to follow stress development of the various films during thermal treatment, a series of in-situ uniaxial stress measurements was made using the force-temperature apparatus. Initial stresses were applied to the samples equivalent to the biaxial drying stresses found earlier. These stresses were determined using the following relationship obtained from linear elasticity:

\[
\sigma_{1D} = (1 - v)\sigma_{2D}
\]  (2.4)
where
\[ \sigma_{1D} = \text{uniaxial stress} \]
\[ \sigma_{2D} = \text{equal biaxial stress} \]
\[ v = \text{Poisson's ratio (}= 0.34 \text{ for polyimide)}. \]

These initial stresses were found to be 7.3, 9.9 and 15.8 MPa respectively for polyamic acid, chemical bath cured and chemical gel cured polyimides respectively. All samples were heated to 320°C with a heating rate of 3 to 5°C/min and the results are shown in figure 2.5. Again, chemical curing using the bath technique has no effect on the final cooling stresses in the polyimide. Chemical curing using the gel technique resulted in lower cooling stresses than both straight thermal curing and chemical bath curing. The slope of the cooling curve was also smaller (-0.052 vs -0.074 MPa/°C).

(Table 2.1) Two-dimensional drying stresses in thermally cured polyimides.

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress (MPa)</th>
<th>Dried at 22°C</th>
<th>After Thermal Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally Cured Polyimide</td>
<td>11 ± 1*</td>
<td>19.77 ± 0.03*</td>
<td>19.81 ± 0.03**</td>
</tr>
<tr>
<td>Bath Cured Polyimide</td>
<td>15 ± 2*</td>
<td>19.2 ± 1.0*</td>
<td></td>
</tr>
<tr>
<td>Gel Cured Polyimide</td>
<td>24 ± 2**</td>
<td>15.62 ± 0.11*</td>
<td>15.15 ± 0.75**</td>
</tr>
</tbody>
</table>

* Measured by holography, ** Measured by membrane deflection.

The effects of the initial stress on thermal stress development were assessed by curing polyamic acid films in the apparatus with initial stresses ranging between 0.1 and 10 MPa. The results of these measurements, shown in figure 2.6, demonstrated that
Figure 2.5) Uniaxial thermal curing stresses measured for polyamic acid, chemical bath cured polyimide and chemical gel cured polyimides.
(Figure 2.6) Uniaxial thermal curing stresses measured for polyamic acid films with different initial stresses.
in all cases the final stress upon cooling to 30°C was unaffected by the initial stress before heating. Figure 2.7 shows multiple thermal cycle imposed on a dried polyamic acid film. Although the cooling stress after each cycle is a function of the highest cure temperature achieved in the previous cycle, the final stress achieved after cooling from 320°C was again approximately 20 MPa. This indicates that for small initial strains the final cooling stress in polyimide films is essentially independent of stress and thermal history and dictated by the highest curing temperature.

It should be noted that if the measured uniaxial cooling stresses are compared to the biaxial stresses measured after thermal treatment using equation 2.4, the biaxial stresses appear to be lower than expected. These lower biaxial stresses are due to thermal expansion of the steel washers to which they are attached. Steel has a TEC of about 10 ppm/°C and, as will be demonstrated, polyimide TEC's lie between 30 and 40 ppm/°C for temperatures between 30 and 300°C. When substrate effects are taken into account, the biaxial stresses increase about 30% becoming consistent with uniaxial measurements.

b. Chemical Curing

In-situ stress measurements during chemical bath cure were performed using the force-swelling apparatus. A polyamic acid sample was placed in the apparatus with an initial stress of 6.5 MPa. The environmental chamber was then flooded with the curing bath solution (1:2:24 acetic anhydride, 3-picoline and cyclohexane) for 40 minutes while the stress was measured with time. The measured stresses are shown in figure 2.8. The stress increased immediately after flooding then decreased slowly over time until the stress disappeared. When the chamber was emptied, the stress increased to 8.7 MPa and did not change with further drying at room temperature. The overall stress increase is consistent with the holographic biaxial stress measurements made earlier.
(Figure 2.7) Uniaxial stresses measured for multiple thermal cycles imposed on polyamic acid.
(Figure 2.8) In-situ measurement of stresses during chemical bath curing of polyamic acid.
The initial stress increase during cure has proved to be something of a puzzle. One explanation may be solvent induced relaxation of stored strain in the polyamic acid film. The amount of shrinkage that occurs in unconstrained polyamic acid films during thermal treatment is an indication that a great deal of stored strain exists in the material as a result of solvent removal. Discussions in Chapter III will reveal that polymeric films do not necessarily need to be above \( T_g \) for significant amounts of stored strain to relax from the material. It is possible that a small amount of solvent in the material can decrease the relaxation times enough for shrinkage to occur. As more solvent enters the material, swelling effects may dominate viscoelastic shrinkage causing the stress to decrease.

Biaxial stress development during the drying of a chemically cured gel film was measured using the membrane deflection technique. A chemical gel cured polyimide coating was prepared and removed from the substrate immediately after gelation and clamped between two steel washers (ID: 38 mm, OD: 63.5 mm). Drying stresses were measured using membrane deflection and the solvent content was measured by weighing the entire washer assembly during drying. The resulting stresses verses volume percentage of polymer, shown in figure 2.9, demonstrate that the coating is able to support stress development even at polymer concentrations less than 10 volume %. During the initial stages of drying, the stress appears to be an exponential function of polymer concentration.

2. Material Properties

The difference in cooling stresses between the various polyimide samples indicates variations in the moduli and/or TEC's. The moduli measured on a number of different polyamic acid and polyimide samples are shown in table 2.2. Each value represents an average of 5-10 samples for each material. Although only a 15% increase
(Figure 2.9) Biaxial stresses developed during chemical gel cure measured by membrane deflection.
in modulus was observed between materials before and after thermal treatment, a significant difference was observed between samples constrained and unconstrained during cure. Very little difference was found between thermally and chemically cured films after thermal treatment. However, modulus values were consistently higher for films with smaller thicknesses as evidenced by the values for commercial Kapton®.

(Table 2.2) Tensile moduli of polyimides cured under various conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>Dried at 22°C</th>
<th>After Thermal Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamic Acid</td>
<td>2.80 ± 0.20</td>
<td>3.45 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>[22.5 ± 0.4 μm]</td>
<td>[14.0 ± 0.2 μm]</td>
</tr>
<tr>
<td>Bath Cured Polyimide</td>
<td>2.92 ± 0.10</td>
<td>3.54 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>[14.8 ± 0.6 μm]</td>
<td>[13.3 ± 0.1 μm]</td>
</tr>
<tr>
<td>Gel Cured Polyimide</td>
<td>3.07 ± 0.20</td>
<td>3.33 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>[25.3 ± 0.2 μm]</td>
<td>[22.5 ± 0.1 μm]</td>
</tr>
<tr>
<td>Unconstrained Polyimide</td>
<td>-----</td>
<td>1.39 ± 0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[162 ± 5 μm]</td>
</tr>
<tr>
<td>Kapton® (30 HN)*</td>
<td>-----</td>
<td>3.43 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[8.5 ± 1.0 μm]</td>
</tr>
<tr>
<td>Kapton® (200 HN)*</td>
<td>-----</td>
<td>2.40 ± 0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[51 ± 2 μm]</td>
</tr>
</tbody>
</table>

*Values for Kapton® were made along the machine direction.
Although it was not possible to obtain modulus information for polyamic acid coating prior to vitrification, it was possible to measure tensile moduli for chemically cured gel films immediately after gelation. Moduli were measured as a function of polymer content and are shown in figure 2.10. The behavior of the modulus during drying was very similar to the behavior displayed by the drying stresses and indicates that the modulus is also a strong function of solvent content for polymer concentrations less than 60% by volume.

Density measurements performed on the various films before and after thermal treatments are shown in table 2.3. On comparing the density of polyamic acid (1.32 g/cc) to the fully cured polyimide (1.42 g/cc) and DMAc (0.957 g/cc) it is estimated that the polyamic acid films dried at room temperature still contain about 27% solvent by volume. Chemical curing at room temperature allows more solvent to escape, however the films still posses 6-9% solvent by volume. The difference in solvent content between polyamic acid and chemical bath cured films can also explain the increase in stress observed in polyamic acid films before and after chemical bath treatment (figure 2.8).

(Table 2.3) Densities of polyimides cured under various conditions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Densities (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Thermal Cure</td>
</tr>
<tr>
<td>Polyamic Acid</td>
<td>1.32 ± 0.01</td>
</tr>
<tr>
<td>Bath Cured Polyimide</td>
<td>1.39 ± 0.01</td>
</tr>
<tr>
<td>Gel Cured Polyimide</td>
<td>1.40 ± 0.02</td>
</tr>
<tr>
<td>Kapton® (200 HN)</td>
<td>----</td>
</tr>
</tbody>
</table>
(Figure 2.10) Tensile modulus as a function of volume % polymer during drying of chemically cured polyimide gel.
The densities of the thermally cured polyimides were also found to be slightly less than the chemically cured polyimides after thermal treatment. Since no solvent should be left after thermal treatment, this suggests that thermally cured films have a less order structure (i.e. lower degree of crystallinity) than chemically cured films. The densities of the chemically cured films match those measured for commercial Kapton®.

The greatest property difference between polyimide samples was revealed in the thermal expansion behavior. The TEC's measured for the various thermally treated films are displayed as a function of temperature in figure 2.11. For all curing techniques, the TEC's were found to increase with temperature. The TEC at 30°C for polyimides cured under no constraints was between 40 and 50 ppm/°C that is slightly lower than value typically found for isotropic glassy polymers (50 to 70 ppm/°C)25. Samples thermally cured on constraining substrates showed much lower TEC's between 30 and 35 ppm/°C. These TEC values compare well to thermal expansion studies performed by Numata on PMDA-ODA films constrained and unconstrained during cure26. Although films cured by the chemical bath technique display little difference in TEC's from thermally cured films, polyimides cured by the chemical gel technique showed slightly lower TEC's between 25 and 30 ppm/°C at 30°C. The lower TEC's for chemical gel cured films are consistent with the cooling stress behavior measured earlier for these materials. The thicknesses of each film are listed is table 2.2.

3. Orientation

The out-of-plane birefringences of polyamic acid and chemically cured polyimide gel coatings were measured as a function of polymer content during drying. Coatings were prepared on mirrored glass substrates and the birefringences measured using the reflection technique described earlier. The results of these measurements are shown in figure 2.12. It has been pointed out that since polyimides have a positive optical
(Figure 2.11) In-plane thermal expansion coefficients measured as a function of temperature for polyimides cured by various techniques.
(Figure 2.12) Out-of-plane birefringences of coatings measured during drying.
anisotropy, a negative out-of-plane birefringence indicates that chain backbones are oriented predominantly parallel to the surface of the film. Contrary to the stress and modulus behavior of polyamic acid coatings, orientation in both polyamic acid and gel cured polyimide coatings appears to develop even at polymer concentrations of 15% by volume. Although, the orientation in polyamic acids developed to only about 50% of that observed in the gel films, orientation begins to develop at polymer concentrations similar to those found in the gel films.

4. Gelation

The orientation and thermal expansion behavior observed thus far raises several questions about the nature of the polyimide gels and how different gelling conditions affect orientation development. The polyamic acid stock solution is a liquid and exhibits a viscosity in the range of 3000 poise. However, the gels behave as solids at the same polymer concentrations. A few experiments were performed to characterize some of the gel properties and investigate some of the effects of gelation on orientation development.

The possibility of covalent crosslinking was explored by performing a solubility study on the polyimide gel. Chemically cured polyimide gel films were made then submerged in DMAc at various times after gelation. Most gelled samples were held at room temperature for short periods of time before submersion, but a few films were placed on a hot plate for five minutes before submersion. The results of the study are shown in table 2.4. It was found that films held at room temperature up to 30 minutes after gelation before submersion were soluble but became insoluble to DMAc after 60 minutes or if exposed to temperatures greater than 50°C. Since the gel films behave as solids within 5 minutes after gelation, covalent crosslinking is probably not the cause of this behavior. It is highly probably that strong physical interactions exist in the gel. However, the exact nature of these interactions is unknown.
A number of experiments were performed investigating the influence of imidization prior to solvent removal on material properties. The influence of polymer concentration during gelation was investigated by preparing chemical gel cured polyimide films from stock solutions with 5, 10 and 15 wt% polymer. Results from thermal expansion measurements on these films are shown in figure 2.13. Although no difference in thermal expansion was observed between the 10 and 15% starting materials, the film formed from the 5% stock solution actually showed an increase in its TEC. This increase is probably due to polymer degradation that occurs much more rapidly in less concentrated polyamic acid solutions.

(Table 2.4) Solubility study on chemically cured polyimide gel films.

<table>
<thead>
<tr>
<th>Time After Gelation</th>
<th>Temperature</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 minutes</td>
<td>25°C</td>
<td>Yes</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>Yes</td>
</tr>
<tr>
<td>60</td>
<td>25</td>
<td>No</td>
</tr>
<tr>
<td>240</td>
<td>25</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>No</td>
</tr>
</tbody>
</table>

Drying of the polyimide gel films could be slowed significantly by covering the surface of the films. A large glass slide was placed on top of a gel film just after gelation and left at room temperature for 24 hours. By the time the film was uncovered, little solvent had escaped from the film and the film had a leathery texture. Upon drying and thermally treating in a clamped frame arrangement to biaxially constrain the material, the TEC was measured and found to be about 3 to 5 ppm/°C lower than
(Figure 2.13) Thermal expansion coefficient verses temperature for gel films made from different stock solutions.
those found in other chemical gel cured films. The TEC results are shown in figure 2.14 and suggest that the degree of imidization before solvent removal plays an important part in orientation development.

An attempt was made to produce a straight thermally cured polyimide gel by curing a polyamic acid solution at 200°C under a nitrogen pressure of 1.38 MPa. This reaction was performed in a pressure chamber held at 200°C for one hour. Under these conditions, imidization is capable of occurring without solvent evaporation. However, the product of this reaction was not a gel but a bright orange powder. Upon further investigation it was found that the powder was fully cured polyimide and had an estimated density of 1.46±0.01 g/cc. Further investigations of the powder are discussed in Chapter V.

D. Discussion

1. Thermal Expansion and Orientation

There are two properties that the thermal expansion coefficient displays for all materials. First, the sum of the TEC's in three orthogonal directions of a material is essentially independent of orientation. This can be true for many different materials as well. Most amorphous glassy polymers have bulk TEC's in the range of 150 to 180 ppm/°C while amorphous rubbers are more in the range of 600 ppm/°C regardless of the chemical structure\textsuperscript{26}. Second, there is a strong correlation between orientation and individual linear TEC's. Oriented fibers often have negative TEC's along the axis while having very large TEC's in the transverse directions. Recent studies have even revealed a linear correlation between birefringence and the TEC's for polyimides over a wide range in orientation\textsuperscript{28}. 

53
(Figure 2.14) Thermal expansion coefficient verses temperature for chemically cured polyimide gels. Sample #1 was dried immediately after gelation. Sample #2 was held for 24 hours before drying.
It can easily be demonstrated that if thermal deformations are affine, the linear TEC must be a linear function of the second moments of the orientation distribution. Let \( x_i \) represent an orthogonal Cartesian coordinate system for the macroscopic properties of a material and \( \alpha_{ij} \) represent the thermal expansion tensor for the material in the macroscopic coordinate system. If a chain segment oriented with respect to a different coordinate system, \( \xi_k \), has a thermal expansion tensor given by \( \alpha'_{kl} \) (see figure 2.15) then in order to represent the segmental properties in the macroscopic coordinate system, \( \alpha'_{kl} \) must be rotated into the \( x_i \) coordinate system by:

\[
\alpha''_{ij} = a_{ik}a_{jl}\alpha'_{kl}
\]

(2.6)

where \( a_{ik} \) is the directional cosine matrix between \( x_i \) and \( \xi_k \) given by \( \cos(x_i, \xi_k) \). If the material is composed of \( N \) such segments, each oriented with respect to an individual coordinate system, \( \xi_k^{(n)} \) in an arbitrary orientation distribution, then the properties of the bulk material can be found by averaging the segmental properties over all the individual segments in the macroscopic coordinate system.

\[
\alpha_{ij} = \frac{1}{N} \sum_{n=1}^{N} \alpha''_{ij} = \frac{1}{N} \left( \sum_{n=1}^{N} a_{ik}^{(n)}a_{jl}^{(n)} \right) \alpha'_{kl} = \langle a_{ik}a_{jl} \rangle \alpha'_{kl}
\]

(2.7)

If \( \alpha'_{kl} \) is a diagonal tensor then equation 2.7 reduces to:

\[
\alpha_{ij} = \langle a_{i1}a_{j1} \rangle \alpha'_{11} + \langle a_{i2}a_{j2} \rangle \alpha'_{22} + \langle a_{i3}a_{j3} \rangle \alpha'_{33}.
\]

(2.8)

From the law of cosines, \( \langle a_{ik}a_{jk} \rangle = \delta_{ij} \) where \( \delta_{ij} \) is the Kronecker delta. Combining this with equation 2.8 one finds that the sum of the diagonal components of \( \alpha_{ij} \) and \( \alpha'_{kl} \) is equal and invariant to orientation:

\[
\alpha_{11} + \alpha_{22} + \alpha_{33} = \alpha'_{11} + \alpha'_{22} + \alpha'_{33} = 3\alpha_{\text{mean}}.
\]

(2.9)
(Figure 2.15) Diagram showing microscopic and macroscopic principal axes.
If \( x \) lie along the principal directions of orientation (i.e. the direction of minimum and maximum orientation) in the material then equation 2.8 reduces to:

\[
\begin{align*}
\alpha_{11} &= \alpha'_L - [\langle a_{21}^2 \rangle + \langle a_{31}^2 \rangle](\alpha'_L - \alpha'_T) \\
\alpha_{22} &= \alpha'_T + \langle a_{21}^2 \rangle(\alpha'_L - \alpha'_T) \\
\alpha_{33} &= \alpha'_T + \langle a_{31}^2 \rangle(\alpha'_L - \alpha'_T).
\end{align*}
\] (2.10)

In the case of films, the orientation parameters specify an in-plane orientation, \( \langle a_{21}^2 \rangle \), often referred to as the anisotropy and an out-of-plane orientation, \( \langle a_{31}^2 \rangle \), referred to as the planarity. These parameters are related to the second order orientation function, \( f_{ij} \), by:

\[
f_{ij} = \frac{3\langle a_{ii}^2 \rangle - 1}{2}.
\] (2.11)

For most polymers, the longitudinal segmental TEC, \( \alpha'_L \), is negative. As a result, increasing orientation causes the TEC in the direction of orientation to decrease.

While a strong orientational influence was observed in this study for the TEC, very little change in modulus was observed even though the modulus is also supposed to be orientational dependent. Since the modulus is described by a 4\(^{th}\) order tensor, it should be dependent on the 4\(^{th}\) moment of the orientation distribution that is not necessarily closely linked with the second moment\(^{29}\). As a result, knowledge of the second order orientation function alone does not guaranty any knowledge of properties dependent on the fourth order average such as modulus.

2. Orientation Development During Gel Collapse

Two types of models exist for describing orientation behavior in polymers. The oldest models describe the orientations of rigid rods in affinely deforming matrices.
Models such as the Kratky "Floating Rod" model\textsuperscript{30} and Wilchinsky's "Spherulitic Deformation"\textsuperscript{31} are typically used to describe the orientation of crystalline polymers. However, they can also be used to describe the orientation of end-to-end vectors of random polymer coils. The other orientation models describe the orientation of segments within the polymer backbone and are really extensions of the rigid rod models. The predictions of both of these models for the second order orientation function will be compared to the orientation behavior displayed by polyimide films during gel collapse.

The orientation of an arbitrary vector in a deforming matrix can be described using finite strain theory. Let $dR$ represent the end-to-end vector of a polymer coil in the undeformed state. After deformation, the new end-to-end vector is represented by $dr$ as shown in figure 2.16. If the deformation is affine, the components of the deformed vector, $dx_i$, can be expressed in terms of the components of the undeformed vector, $da_i$, and the principal draw ratios, $\lambda_i$, describing the deformation.

\[
dx_i = \lambda_i da_i \quad \text{(no sum)} \tag{2.13}\n\]

According to Lagrangian finite strain theory, the $dr^2$ is related to $da_i$ through the right Cauchy-Green deformation tensor, $C_{ij}$.

\[
dr^2 = C_{ij} da_i da_j \tag{2.14}\n\]

Dividing both sides of equation 2.14 by $dR$ one finds that the length change of $dR$ is related to the orientation of $dR$ through the angles, $\Theta_j$, with respect to the principal directions of deformation.

\[
\frac{dr^2}{dR^2} = C_{ij} \frac{da_i da_j}{dr dr} = \lambda_1^2 \cos^2 \Theta_1 + \lambda_2^2 \cos^2 \Theta_2 + \lambda_3^2 \cos^2 \Theta_3 \tag{2.15}\n\]

The orientation angles in the deformed state are related to the angles in the deformed state ($\Theta_j$) through equation 2.16.
Before Deformation

After Deformation

(Figure 2.16) Components of an end-to-end vector before and after deformation.
\[ \cos^2 \theta_i = \frac{dx_i^2}{da_i^2} \frac{dR^2}{dr^2} \cos^2 \theta_i \]  

(2.16)

Substituting equation 2.15 into equation 2.16 and applying the law of cosines, the orientation of the deformed vector can be related to the orientation of the undeformed vector on the principal draw ratios:

\[ \cos^2 \theta_i = \frac{\lambda_1 \cos^2 \Theta}{(\lambda_1 \cos^2 \Phi + \lambda_2 \sin^2 \Phi + \lambda_3 \sin^2 \Theta)} \]  

(2.17)

where \( \Theta \) and \( \Phi \) are related to \( \theta_i \) by:

\[
\begin{align*}
\cos \Theta_1 &= \sin \Theta \cos \Phi \\
\cos \Theta_2 &= \sin \Theta \sin \Phi \\
\cos \Theta_3 &= \cos \Theta,
\end{align*}
\]

The average orientation of a distribution of arbitrary vectors can be found by integrating equation 2.17 over all values of \( \Theta \) and \( \Phi \) with a distribution function, \( N(\Theta, \Phi) \), describing the state of orientation prior to deformation.

\[
f_{ii} = \frac{1}{8\pi} \int_0^{2\pi} \int_0^\pi (3\cos^2 \theta_i - 1)N(\Theta, \Phi) \sin \Theta \, d\Theta d\Phi
\]

(2.18)

If the material is initially isotropic before deformation, then \( N(\Theta, \Phi) = 1 \). For a uniaxial deformation with no dilatation:

\[ \lambda_3 = \lambda \quad \text{and} \quad \lambda_1 = \lambda_2 = 1/\lambda^{1/2}. \]

(2.19)

Substituting into equation 2.18 one finds:
\[ f_{33} = \frac{1}{4} \int_{0}^{\pi} \frac{\lambda^3 (3\cos^2 \Theta - 1) \sin \Theta \ d\Theta}{\lambda^3 + (1 - \lambda^3)\cos^2 \Theta} . \] 

(2.20)

This result is equivalent to the Spherulitic Deformation model proposed by Wilchinsky\textsuperscript{32}.

Equation 2.20 describes the large scale random coil orientation behavior during deformation. The segmental orientation is found by averaging over the combined orientational distribution functions for end-to-end orientation and segmental orientation with respect to the end-to-end vector. In 1942, Kuhn and Grun derived the orientation distribution function for segments of a polymer coil with respect to a uniaxially deformed end-to-end vector\textsuperscript{32}:

\[ n(\chi, \varphi) = \frac{\beta}{\sinh \beta} e^{\beta \cos \chi} \] 

(2.21)

where

\[ \chi, \varphi = \text{angles describing segmental orientation w.r.t. deformation axis in spherical coordinates} \]

\[ \beta = \mathcal{L}^{-1}[(dr)/nL] \]

\[ \mathcal{L}[x] = \text{Langevin function} = \coth x - 1/x \]

\[ n = \text{number of freely jointed segments} \]

\[ L = \text{segment length}. \]

The end-to-end vector distribution function in the deformed state can be found from equation 2.20. The resulting distribution function is:

\[ N(\theta, \phi) = \frac{\lambda^3}{[\lambda^3 + (1 - \lambda^3)\cos^2 \theta]^{3/2}}. \] 

(2.22)

Roe and Krigbaum combined the two distribution functions and derived expressions for various orientation functions with aid of spherical harmonic expansions\textsuperscript{33}. The
expression describing the behavior of the second order orientation function during
constant volume uniaxial deformation was:

\[ f_{33} = \frac{1}{5n} [\lambda^2 - 1/\lambda] + \frac{36}{75n^2} [\lambda^4 - \lambda/3 - 4/(3\lambda^2)] \\
+ \frac{108}{6125n^3} [\lambda^6 - 3\lambda^3/5 - 8/(5\lambda^3)] + O(\lambda^8,n^4). \] (2.23)

The gel collapse process imposes two types of deformation on the material. Solvent loss itself produces a dilatational deformation while the constraining substrate induces a distortional deformation in the material. Since pure dilatation does not affect macroscopic orientation, only the distortional component of gel collapse contributes to orientation development in coatings. This distortional component can be found by breaking the collapse process up into two stages as shown in figure 2.17.

The first stage consists of the dilatational component of gel collapse. During this stage, all dimensions of the initial coating are reduced by a factor, \( \alpha \), that is related to the volume changes in the coating by:

\[ \alpha^3 = \left( \frac{V}{V_0} \right) = \left( \frac{\phi_0}{\phi_p} \right) \] (2.24)

where

- \( V \) = volume of coating
- \( V_0 \) = volume of coating at gelation
- \( \phi_p \) = volume fraction of polymer in coating
- \( \phi_0 \) = volume fraction of polymer at gelation.

The second stage of gel collapse contains the distortional component of deformation. During this process, the in-plane dimensions of the coating are restored to their original values and the thickness of the coating is reduced again by a factor, \( \lambda \). The term, \( \lambda \), describes a uniaxial compression in the thickness direction and can be used directly in equations 2.20 and 2.23. Since no dilatation occurs during the
(Figure 2.17) Schematic of dilatational and distortional components of deformation during gel collapse.
stretches process, \(\lambda\) is equal to \(\alpha^2\) and can be related to the polymer concentration in the coating by:

\[
\lambda = \left(\frac{V}{V_0}\right)^{2/3} = \left(\frac{\phi_P}{\phi_p}\right)^{2/3}.
\]

Figure 2.18 shows the predictions of the end-to-end vector and the segment orientation during gel collapse for coils with different values of \(n\). Although the end-to-end orientation behavior appears to be independent of molecular weight and stiffness effects, the segmental orientation does appear to be very dependent on the number of segments between crosslinks. The birefringence measurements shown in figure 2.12 compare well with the segmental orientation model. The similarity of the measured birefringence data with the segmental orientation predictions suggests that the increased orientation in gel cured polyimides is probably a result of increased chain stiffness from chemically curing. Increased chain stiffness may also account for the lower TEC's observed for gel cured films held at room temperature before drying and are consistent with studies on the influence of chain stiffness on thermal expansion behavior\(^{34}\).

E. Conclusions

The main conclusion of this study is that chemically curing can alter the stress behavior in polyimide films by inducing greater orientation during solvent removal. Results from orientation measurements and theoretical models both suggest that the source of the increased orientation is an increase in the chain stiffness of polyamic acid molecules prior to solvent removal. The increased stiffness then increases the ability of polymer chains to orient during solvent removal. Since thermal expansion depends on
(Figure 2.18) Predictions for end-to-end and segmental orientation behavior during drying after gelation at 10 volume % polymer.
orientation, orientation predictions suggest that one way to lower in-plane TEC's is to increase the amount of imidization in polyamic acids prior to solvent removal. TEC's were reduced slightly by varying the rate of solvent removal and the effects of curing polyimides under moderate pressure to prevent solvent removal during will be discussed in Chapter V.

It should be pointed out that although in-plane TEC's can be reduced by orientation, these reductions are made at the expense of TEC's in the thickness direction. Since polyimide films are being used more often in multilayered structures, the problems of out-of-plane thermal expansion is becoming more prominent. This suggests that if a balance cannot be struck between in and out-of-plane thermal expansion behavior, the next stages of investigations should concentrate on finding means of reducing the volumetric thermal expansion behavior of polymers.
References


28. Edman, J.R., Coburn, J.C., and Pottiger, M., To be Published.


30. Kratky, O., "Zum Deformationsmechanismus der Faserstoffe, I.", Kolloid Z., 64, 213 (1933)


CHAPTER III
CHARACTERIZATION OF DIMENSIONAL INSTABILITY IN POLYIMIDE FILMS

A. Introduction

1. Motivation

Most polymeric materials exhibit irreversible shrinkage in one form or another. Although irreversible shrinkage is often a useful property in polymers, it is more often a problem in electronics applications where the maintenance of strict dimensional stability is important. Shrinkage behavior is most often evident under conditions where material properties change rapidly such as during phase transitions. However, shrinkage can also be closely tied to the stress history of materials as well. Blumentritt demonstrated that the principal directions of shrinkage in Kapton® polyimide films lie at ±45° to the machine direction. Analyses in Chapter IV will demonstrate that the principal directions of stress during the processing of Kapton® also lie at ±45° to the machine direction and correspond closely to shrinkage as well.

The purpose of this investigation is to characterize irreversible shrinkage behavior and lay the foundations for developing a quantitative relationship between irreversible shrinkage and stress history. Such a relationship would be useful for a number of reasons. First, this relationship would allow for the prediction of irreversible shrinkage, a feat which is currently not possible on a general basis, and aid in finding ways to control such behavior. Second, it may be possible to use irreversible shrinkage as a source of information about processing stresses under conditions where
measurement is difficult. Lastly, shrinkage behavior may also provide easily obtained information about the constitutive properties of various materials.

The first part of this investigation will be a qualitative characterization of the effects of stress and thermal history on the shrinkage behavior displayed by polyimides. A thermal cycling technique will then be introduced which allows quantitative measurement of shrinkage behavior in materials under well-characterized stress and thermal histories simulating those encountered during film processing. A brief discussion will be given on the use of incremental elasticity and linear viscoelasticity for modeling shrinkage behavior. Measurements of constitutive properties will then be used to predict shrinkage behavior found in polyimide films.

2. Residual Stress versus Stored Strain

Before a discussion of irreversible shrinkage can begin, it is necessary to make a distinction between "residual stress" and "stored strain". Shrinkage behavior is usually attributed to the existence of residual stresses in materials. This terminology is most often used in injection molding circles where the use is most often correct. However, the term: "residual stress" may actually be a misnomer when describing the shrinkage behavior of many materials.

Continuum mechanics describe stress as the result of a force vector acting on a surface element. Since stresses are continuous functions and must also satisfy a force balance in the form of the equilibrium equations, it is impossible to have a free standing article under purely tensile or compressive residual stresses in the absence of body forces. All tensile residual stresses in a free standing material must be balanced by compressive stresses at some other point in the material. This phenomenon is commonly observed in many materials such as in thermally quenched materials where rapid cooling creates compressive residual stresses at surfaces while causing tensile
stresses to develop in the bulk. Residual stresses are also observed in coating parts which develop tensile stresses while producing compressive stresses in the underlying substrates.

Since all residual stresses must be balanced, these stresses must vary from point to point throughout materials. These stresses exist on a continuum level and are measurable. If a material that contains residual stress is cut into small enough pieces, each piece will change its dimensions slightly but each not in the same way. Some experimental methods are based on this principal for the measuring of residual stresses. However, some materials that exhibit shrinkage behavior do not exhibit any stresses on a continuum level prior to shrinkage. The state of stress is both homogenous and zero throughout the material. Although these materials possess a higher potential energy prior to shrinkage, this energy is sustained by forces on a molecular scale. Calling these forces 'residual stresses' violates the fundamental postulate of continuum mechanics and is analogous to calling ideal solutions phase separated on a molecular scale.

Although the materials discussed in this study do not exhibit residual stresses, they still possess extra potential energy prior to shrinkage in the form of strains. The terms: "stored strain" or "frozen-in strain" will be adopted in this study for the description of this potential energy.

B. Experimental

1. Materials

Two different polyimide films were used at various points in this study. Spin coated PMDA-ODA polyimide films were made from a 15 wt% solution of poly-[N,N'-bis-phenoxyphenyl pyromellitamic acid] in dimethylacetamide obtained from duPont.
Samples were made by spin coating the solution onto 5 inch by 5 inch glass plates and drying at 100°C on a hot plate for 1 hour. The samples were then placed in a vacuum oven for one hour to complete the second stage of cure. Most samples were cured at 450°C. The second film studied was Upilex-R®, a commercial form of biphenyl dianhydride-oxydianyline (BPDA-ODA) produced by Ube® Industries.

Crosslinked epoxy films were also investigated briefly in this study. These were made from a 5:4 weight ratio of Epon 828® and V40® amine. The two components were mixed then spun coated onto tin coated steel plates. The plates were placed on a hot plate at 50°C for a half hour to eliminate air bubbles then cured at 200°C under vacuum. The films were then placed in a mercury bath to remove the films from the substrate. Further description of film removal can be found in Chapter II. The chemical structures of all materials used in this study are listed in table 3.1.

2. Shrinkage Measurements

All shrinkage experiments were performed on a TA Instruments® 2940 Thermal Mechanical Analyzer (TMA) fitted with a film and fiber attachment. In the film and fiber mode, samples with a length of 25.4 mm and width of 1-3 mm are held vertically and under tension by a quartz probe. This is shown in figure 3.1. Forces are applied to the sample by means of a calibrated electromagnet located around the bottom of the probe allowing versatile control over forces between 0.001 and 1.000 N. A computer controller allows the possibility of changing forces during experiments and of performing isostrain experiments in limited cases as well. All heating runs were performed at 5°C/min under loads between 0.001 and 0.003 N. Samples are air cooled by the instrument. Although 5°C/min cooling rates could be achieved for temperatures greater than 90°C, the cooling rates slowed to about 0.5 to 1°C/min at 30°C. Isostrain
(Figure 3.1) Schematic of TA Instruments 2940 Thermal Mechanical Analyzer in the film and fiber mode.
cooling stages during controlled shrinkage cycles were performed by manually changing the force settings every 5°C during cooling.

(Table 3.1) Chemical structures of materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
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<td>Kapton® (PMDA-ODA):</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Upilex-R® (BPDA-ODA):</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Epon 828®:</td>
<td><img src="image" alt="Chemical structure" /></td>
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</tbody>
</table>

3. **Material Property Measurements**

All material properties were measured in this study using the TMA described above. Thermal expansion coefficients were determined by calculating linear regression slopes of the strain verses data over a ±10°C range. TEC measurements were only measured during cooling or during second passes to eliminate shrinkage effects.
Equilibrium moduli were obtained using the impulse viscoelasticity technique described by Vratsanos and Farris (1987). Load pulses were applied to the materials at different temperatures and the areas under the load and strain versus time curves were measured using the TA Instruments TMA Data Analysis software. The equilibrium moduli, $E_{eq}$, could be obtained from the ratio of the stress-time and strain-time integrals as shown in equation 3.1:

$$E_{eq} = \frac{\int_{0}^{\infty} \sigma(t) \, dt}{\int_{0}^{\infty} \varepsilon(t) \, dt}$$

All values represent an average of five pulses.

Viscoelastic analysis of PMDA-ODA and Upilex-R® films involved performing isothermal creep experiments on the films at different temperatures. Samples were first annealed in the TMA at 450°C for PMDA-ODA films and 350°C for Upilex-R® films. The samples were then held at various temperatures for 30 minutes to establish a baseline then subjected to a step increase in stress of about 5 MPa. PMDA-ODA samples were held for approximately 3 hours at each temperature and Upilex-R® samples for 6 hours. The stresses applied to the Upilex-R® films were reduced to 1 MPa at temperatures above 240°C in order to keep displacements within the measurable range of the TMA (±3 mm). The unshifted compliance values could then be found by:

$$D(t) = \frac{\varepsilon(t)}{\sigma_0}$$

where $\varepsilon(t)$ was referenced with respect to the thermal strain at each temperature.
C. Shrinkage Characterization

1. Shrinkage in Spin Coated Polyimides

Figure 3.2 demonstrates shrinkage behavior typically observed in polyimide films. A PMDA-ODA polyimide film was prepared by spin coating onto a glass substrate and curing at 400°C. Immediately after cooling, the film was removed from the substrate and a sample from the film was subjected to two unconstrained thermal cycles between 30 and 400°C in the TMA. The most evident feature in the strain verses temperature data is an apparently lower thermal expansion of the film during heating in the first cycle than on cooling. This behavior continues until approximately 380°C when the material actually begins to shrink. The overall shrinkage as a result of the cycle was approximately 1%. When the material is heated again to the same temperature, no shrinkage occurs and the thermal expansion behavior is reversible.

In order to investigate the effects of temperature on shrinkage behavior, a number of different unconstrained thermal cycles were imposed on another PMDA-ODA polyimide film cured at 300°C. Two samples were taken from the film and subjected to slightly different thermal cycles. The first sample was subjected to one cycle between 30 and 320°C resulting in a total shrinkage of approximately 1.1%. The second sample was subjected to five cycles with successively higher temperatures. The highest temperatures on each pass were: 150, 200, 250, 300 and 320°C. The resulting shrinkage behavior is shown in figure 3.3. During the first cycle, the film shrank approximately 0.1% during heating. During the next cycle, the strain behavior of the material during heating followed the same path as the strain during cooling in the previous cycle until the temperature approached 150°C. From 150 to 200°C the film shrank another 0.1%. This process continued for the next three cycles resulting in an overall shrinkage of approximately 1.1% for all five cycles. The total shrinkage behavior
(Figure 3.2) Strain verses temperature for spin coated PMDA-ODA polyimide film cured at 400°C.
(Figure 3.3) Strain versus temperature for spin coated PMDA-ODA polyimide film cured at 300°C. Sample #1 was subjected to one cycle to 320°C. Sample #2 was subjected to multiple cycles to 150, 200, 250, 300 and 320°C.
displayed by the film during the multiple thermal cycles was identical to the behavior of the material during the single cycle.

In order to assess the effects of shrinkage on stress development, similar heating cycles were imposed on the 300°C cured polyimide under isostrain conditions. The results are shown in figure 3.4. As expected, the stress behavior followed the shrinkage behavior. During the first cycle, the stress on heating was zero due to sample buckling from thermal expansion. Upon cooling, tensile stress did not develop in the films until approximately 70°C. This temperature also corresponds to the temperature during the unconstrained thermal cycling experiments (figure 3.3) where the strain first drops below 0%. This occurred for succeeding cycles as well.

The examples discussed above demonstrate a strong relationship between shrinkage behavior and temperature. In each case, shrinkage occurs gradually at temperatures below the curing temperature. This behavior coincides with the development of curing stresses in this material as discussed in the last chapter. However, the sharp increases in shrinkage behavior at temperatures approximately 20°C below the cure temperatures of each material also indicate a strong influence from the behavior of mechanical properties in the material as well. It is generally believed that the glass transitions of polyimides closely follow the cure temperatures of these materials\(^3\). This is consistent with the shrinkage behavior observed so far in this study.

It has also been suggested that PMDA-ODA materials have a true glass transition near 400°C\(^4\). In an attempt to observe this transition, a spin coated PMDA-ODA film was cured at 450°C and subjected to two unconstrained temperature cycles between 30 and 450°C. Surprisingly, the resulting shrinkage behavior, shown in figure 3.5, revealed no evidence of a transition at below 450°C. However, no transition behavior was observed at 450°C either. If one observes the transitions regions in the polyimide films cured at 300 and 400°C, one notices that the magnitude of the shrinkage occurring at the cure temperatures appears to decrease with increasing
(Figure 3.4) Stress verses temperature for spin coated PMDA-ODA polyimide cured at 400°C.
(Figure 3.5) Strain verses temperature for spin coated PMDA-ODA cured at 450°C.
temperature. It may be possible that the amount of shrinkage occurring due to a true glass transition in this material is too small to be observed by this technique.

2. **Controlled Shrinkage Cycles**

In order to separate the effects of material properties and stress history it is necessary to observe shrinkage behavior in materials with well-characterized stress histories. A technique was developed that simulates the stress history that polyimides undergo during cure and predicts the resulting shrinkage from this stress history. In this technique, a sanferized sample is subjected to a series of thermal cycles shown in figure 3.6. A polyimide sample cured at 400°C and sanferized at 450°C is first heated to 300°C under near zero stress conditions as indicated by points 0 to 1 in figure 3.6a. The sample is then cooled to 30°C under constant strain conditions designated by points 1 to 2. The stress that develops during this stage is shown in figure 3.6b. Immediately after the sample reaches 30°C the resulting stress is suddenly released (points 2 to 3). After the stress is released the sample does not return to its original length but shows an overall length increase of about 0.4%. The length increase represents the stored strain in the sample as a result of the cooling stress history. After stress release, the sample was immediately reheated to 350°C then cooled back to 30°C as indicated by points 3 through 5. The shrinkage behavior displayed by the sample during the last cycle is very similar to that displayed by the spin coated polyimides below the cure temperature.

A similar cycle was applied to a similar PMDA-ODA sample in order to observe shrinkage with time after stress release. This cycle is shown in figure 3.7. This cycle is identical to the cycle shown in figure 3.6 accept that the sample was held for 24 hours at 30°C after the stress release between points 2 and 3. This experiment demonstrates that shrinkage does occur with time but decreases exponentially. In a 24 hour period the film shrank about 0.1%. Although figure 3.7c demonstrates that the material clearly had
(Figure 3.6) Part (A): Strain verses temperature resulting from controlled shrinkage experiment. (0 to 1 - heating under zero stress, 1 to 2 - isostrain cooling, 2 to 3 - stress release, 3 to 4 - heating under zero stress, 4 to 5 - free shrink cooling)
Part (B): Stress verses temperature during isostrain cooling of controlled shrinkage experiment
(Figure 3.7) Part (A): Strain versus temperature resulting from controlled shrinkage experiment. (0 to 1 - heating under zero stress, 1 to 2 - isostrain cooling, 2 to 3 - stress release with 24 hr isotherm, 3 to 4 - heating under zero stress, 4 to 5 - free shrink cooling)

Part (B): Stress versus temperature during isostrain cooling of controlled shrinkage experiment.

Part (C): Strain versus time during isothermal stage after stress release.
not reached equilibrium after 24 hours, significant additional shrinkage would require a
time frame much larger than 24 hours.

In order to assess the effects of glass transition temperatures on shrinkage,
similar cycles were also imposed on an epoxy film (T_g ~ 80°C) and Upilex-R® film (T_g ~
260°C). The results of these experiments, shown in figures 3.8 and 3.9, show a strong
correlation between the glass transition temperature and shrinkage behavior similar to
that seen in PMDA-ODA around the cure temperature.

Goldfarb and Farris demonstrated that polyimide films permanently stretched as
much as 30% at room temperature recover completely when heated. In order to
further investigate this behavior, polyimide films cured and sanferized at 400°C were
stretched at different temperatures to observe shrinkage behavior upon reheating.
Figures 3.10 and 3.11 show the stress-strain and shrinkage behavior of films stretched
to 5% at 22 and 240°C. Strains were applied and released at a rate of 1% per minute.
The stress verses strain curves demonstrated considerable hysteresis resulting in
permanent deformations of about 0.5% at both 22 and 240°C. Upon reheating, the
sample stretched at 22°C began recovery immediately when heated above room
temperature while the sample stretched at 240°C did not demonstrate any shrinkage
behavior until above 220°C.

D. Modeling Shrinkage Behavior

1. Constitutive Equations

The basic requirement for a constitutive equation allowing strain storage is that
it must allow the properties of the material to change during the course of history. The
simplest such constitutive equation is given by incremental elasticity theory. As
(Figure 3.8) Part (A) Strain versus temperature resulting from controlled shrinkage cycle on Epon 828 / V40 epoxy.
Part (B) Stress versus temperature during isostrain cooling of controlled shrinkage cycle.
(Figure 3.9) Part (A) Strain verses temperature resulting from controlled shrinkage cycle on Upilex-R® film.
Part (B) Stress verses temperature during isostrain cooling of controlled shrinkage cycle.
(Figure 3.10) Stress verses strain curves for samples stretched at 22 and 240°C.

(Figure 3.11) Strain verses temperature for polyimide samples stretched at 22 and 240°C.
described in the last chapter, incremental elasticity is an incremental form of linear
elasticity. Material properties are assumed to be constant over incremental changes in
strain or processing conditions. However, the properties may change from increment
to increment. The overall response of the material to a given process can be found by
summing up all of the individual increments.

Strain storage predictions can be made from incremental elasticity by applying
the constitutive equation to the controlled shrinkage cycles described in the last section.
A schematic of the first three stages of this cycle is shown in figure 3.12. During the
first stage, the samples are heated under essentially zero stress conditions (points 0 to
1). The strain expressed by incremental elasticity is:

\[ \varepsilon_1 = \frac{T_h}{T_0} - \int \alpha dT \]  

(3.2)

where \( T_h \) and \( T_0 \) are the upper and lower temperatures achieved in the cycle and \( \alpha \) is the
temperature dependent thermal expansion coefficient. During the second stage, the
sample is cooled under constant strain and a stress develops in the material given by:

\[ \sigma_2 = -\frac{T_0}{T_h} \int \alpha E dT \]  

(3.3)

where \( E \) is the temperature dependent modulus of the material. During the third stage,
the stress in the material is released. The resulting strain on the material is:

\[ \varepsilon_3 = \varepsilon_1 - \int_{\sigma_2}^{\sigma_2} \frac{1}{E_0} d\sigma = \varepsilon_1 - \frac{\sigma_2}{E_0} \]  

(3.4)

90
Strain

Temperature

(Figure 3.12) Schematic of controlled shrinkage cycles.
where $E_0$ is the modulus at $T_0$. Combining equations 3.2 through 3.4, one finds that the overall length of the sample increases after the third stage. The resulting stored strain is $\varepsilon_3$ given by:

$$
\varepsilon_3 = \int_{T_0}^{T_h} \alpha (1 - \frac{E}{E_0}) dT = \varepsilon_i^0 - \frac{\sigma_i}{E_0}.
$$

(3.5)

This relation indicates that strain storage occurs due to the presence of a temperature dependent modulus.

Figure 3.13 shows the thermal expansion coefficients and equilibrium moduli measured for the spin coated polyimide film cured at 400°C. Using this data in equation 3.4, a stored strain of about 0.3% is predicted from an isothermal cooling from 300°C to 30°C. This amount is very similar to the amount of stored strain actually measured in polyimide shown figure 3.5. The final cooling stress calculated from equation 3.2 was approximately 21 MPa which is slightly higher than the measured stress of 15 MPa.

Although incremental elasticity appears to give accurate predictions of stored strain, it has a serious shortcoming in that it cannot predict shrinkage behavior. It is possible for strain to be stored in incrementally elastic materials. However this stored strain can never be released. When the materials with stored strain are heated again, they expand due to normal thermal expansion but no shrinkage occurs. This is illustrated in figure 3.14.

The next class of constitutive equations that can be used to describe stored strain and shrinkage is provided by thermoviscoelasticity. The general equations of linear thermoviscoelasticity for rheologically simple materials are:
(Figure 3.13) Thermal expansion coefficient and equilibrium modulus for spin coated polyimide cured at 400°C.
(Figure 3.14) Schematic of incremental elasticity predictions for controlled shrinkage cycles.
\[ \sigma(t) = \int_{0}^{\xi(t)} E(\xi - \zeta) \frac{d}{d\zeta} [\varepsilon(\zeta) - \varepsilon(\zeta)] d\zeta \]

\[ \varepsilon(t) = \varepsilon(\zeta) + \int_{0}^{\zeta(t)} D(\xi - \zeta) \frac{d\sigma(\zeta)}{d\zeta} d\zeta \]

where

\[ \xi(t) = \int_{0}^{\varepsilon(\zeta)} \alpha(\xi - \zeta) \frac{\partial T(\zeta)}{\partial \zeta} d\zeta \]

The terms: \( E(\xi) \), \( D(\xi) \) and \( \alpha(\xi) \) are the time dependent modulus, compliance and thermal expansion coefficient. The terms: \( \xi \) and \( \zeta \), are referred to as reduced times and are monotonically increasing functions of the temperature dependent shift function, \( \alpha_T \), and the thermal history:

\[ \xi = \int_{0}^{t} a( \eta ) [T(\eta)]^{-1} d\eta \]

\[ \zeta = \int_{0}^{\tau} a( \eta ) [T(\eta)]^{-1} d\eta \]

where \( 0 \leq \tau \leq t \).

Although most materials exhibit time dependent thermal expansion coefficients in the form of densification, the effects of this behavior will not be considered in this study. As a result, the thermal expansion coefficient will be assumed to be a time independent function of temperature and the strain due to thermal expansion, \( \varepsilon(\xi) \), can be expressed as:
For a further discussion of thermoviscoelasticity, a good reference is Christiansen's *Theory of Viscoelasticity: An Introduction*. In order to calculate stored strain and shrinkage predictions from viscoelasticity, it is necessary to obtain thermal and viscoelastic characterizations of the materials in question. This characterization will be discussed next.

2. Material Characterization and Data Analysis

The viscoelastic calculations to be described later in this chapter required the expression of constitutive properties in terms of analytical functions. This section will describe the measurement and function fitting of thermal and viscoelastic properties measured for PMDA-ODA and Upilex-R® films.

a. Thermal Expansion

The temperature dependent thermal expansion coefficients for PMDA-ODA are shown in figure 3.13. This data was hand fitted with a function form: $\alpha(T) = k/(f - dT)$ where $k$, $d$, and $e$ are fitting parameters. The parameters that best fit the data were: $k = 0.0798$ ppm, $d = 5$ and $f = 2850^\circ$C.

Figure 3.15 shows the thermal expansion coefficients verse temperature behavior for Upilex-R®. This data was fitted with two functions. For temperatures less than 280°C, the TEC was fitted with: $\alpha(T) = A + B*(T-30^\circ$C) + Ce$^{M(T-273^\circ$C)}. For temperatures greater than or equal to 280°C, the TEC was fitted with: $\alpha(T) = F(T-$
(Figure 3.15) Thermal expansion coefficient verses temperature for Upilex-R® films.
The parameters that best fit this data were: $A = 22 \text{ ppm/°C}$, $B = 0.0794 \text{ ppm/°C}^2$, $C = 28.75 \text{ ppm/°C}$, $M = 0.055 \text{ °C}^{-1}$, $F = 57 \text{ ppm/°C}$ and $N=0.2$.

**b. Time-Dependent Compliances and Shift Functions**

The unshifted compliance data for PMDA-ODA and Upilex-R® are shown in figures 3.16 and 3.17. Time-temperature shifting of the compliance data was performed using a combination of visual and error minimization techniques. For the PMDA-ODA samples and the Upilex-R® samples below 255°C, the compliance master curve was fitted to a power law function of the form: $D(t) = A + Bt^m + Ct^n$, where $A$, $B$, $C$, $m$ and $n$ are fitting parameters. Error minimization of the power law function could be performed to obtain values for $A$, $B$ and $C$ with initial guesses of $m$ and $n$. The shifting procedure used was as follows. First, the compliance data was shifted by hand. A computer code, listed in Appendix C, was used to calculate $A$, $B$, $C$ and an error coefficient for a range of $m$ and $n$ values. The error coefficient, $S_R$, was defined as:

$$
S_R = \sum_{i=1}^{N} [D_i - D(t_i)]^2
$$

(3.9)

where $t_i$ and $D_i$ are the shifted time and compliance data. The coefficients $m$ and $n$ were then chosen as the combination that produced the lowest fitting error. Several estimates at data shifting were used to obtain shifted data with the lowest overall fitting error. Compliance data for the Upilex-R® samples above 255°C were shifted by hand with no error minimization. The full range Upilex-R® master curve was then fitted with another analytical function of the form: $D(t) = bt^n + c\left(1 - \frac{1}{1 + at^t}\right)t^t$ to aid in later shrinkage calculations. The shifted compliance data and fitting coefficients are shown in figures 3.18 and 3.19. The regression coefficient, $R$, is defined as: $R = \sqrt{\frac{S_t - S_R}{S_t}}$
(Figure 3.16) Time-dependent creep compliances measured for spin coated PMDA-ODA polyimide films.

(Figure 3.17) Time-dependent creep compliances measured for Upilex-R® polyimide films.
(Figure 3.18) Shifted time-dependent creep compliances for spin coated PMDA-ODA polyimide films.

(Figure 3.19) Shifted time-dependent creep compliances for Upilex-R® polyimide films.
where \( S_i = \sum_{i=1}^{N} [D_i - \langle D(t_i) \rangle]^2 \). The brackets \( <> \) designate an average over the fitted compliance.

Figures 3.20 and 3.21 show \( \log(a_T) \) verses temperature for both PMDA-ODA and Upilex-R\textsuperscript{®}. Below \( T_g \), \( \log(a_T) \) displayed roughly a first order dependence on the temperature for materials. The shift function for Upilex-R\textsuperscript{®} above 255°C could be fitted very well using the WLF Equation with the "universal constants"\textsuperscript{7}. This is shown in figure 3.21. An estimate \( T_g \) of 262°C was obtained for Upilex-R\textsuperscript{®} based on the fit of the WLF equation.

c. Time-Dependent Moduli

The moduli master curves could be found from the compliance master curves through the relationship: \( \overline{D}(s)\overline{E}(s) = 1/s^2 \) where \( \overline{D} \) and \( \overline{E} \) are the Laplace transforms of the compliance and modulus master curves respectively and \( s \) is the variable in Laplace space. Although performing Laplace transforms on power law functions is a simple matter, obtaining inverse Laplace transforms is not a straightforward process. It is possible to obtain inverse Laplace transforms of exponential functions. As a result, the compliance master curves were fitted to a second function of the form:

\[
D(t) = D_0 + D_1(1 - e^{t/\tau_1}) + D_2(1 - e^{t/\tau_2}) + ... + D_n(1 - e^{t/\tau_n}) \quad (3.10)
\]

where \( D_i \) and \( \tau_i \) are fitting parameters often referred to as the retardation coefficients and the retardation times. The Laplace transform of equation 3.10 is:

\[
\overline{D}(s) = \frac{1}{s} \sum_{i=0}^{n} D_i \frac{D_1}{s + 1/\tau_1} - D_2 \frac{D_2}{s + 1/\tau_2} - ... - D_n \frac{D_n}{s + 1/\tau_n} \quad (3.11)
\]

and the transform of the modulus becomes:

\[
\overline{E}(s) = \left( \frac{s D_1}{s + 1/\tau_1} - \frac{s D_2}{s + 1/\tau_2} - ... - \frac{s D_n}{s + 1/\tau_n} \right)^{-1} \quad (3.12)
\]
(Figure 3.20) Shift function for PMDA-ODA polyimide film.

\[ \log(aT) = 0.3980T - 0.03892 \]
\[ R = 0.98307 \]

(Figure 3.21) Shift function for Upilex-R® film.

\[ T < 255^\circ C: \]
\[ \log(aT) = 0.5024 - 0.0607T \]
\[ T > 255^\circ C: \]
\[ \log(aT) = -18.5 - \frac{17.4(T - 262^\circ C)}{51.6 + T - 262^\circ C} \]
If equation 3.12 is broken up into partial fractions, the inverse Laplace transform can be performed to obtain the master curve for the time-dependent modulus in the form:

\[ E(t) = E_o + E_1 e^{-\tau_1} + E_2 e^{-\tau_2} + \ldots + E_n e^{-\tau_n} \]  

(3.13)

where \( E_i \) and \( \tau_i \) are the relaxation coefficients and relaxation times. A computer code was written, using the partial fraction routine, to obtain the time-dependent modulus master curve. This code is listed in Appendix D. The retardation and relaxation coefficients and times for the PMDA-ODA and Upilex-R® films are shown in tables 3.2 and 3.3.

(Table 3.2) Retardation and relaxation coefficients and times for PMDA-ODA film.

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<th>i (MPa)</th>
<th>( \tau_i ) (sec)</th>
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(Table 3.3) Retardation and relaxation coefficients and times for Upilex-R® film.

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The modulus master curves were then fitted once again to power law functions of the forms: \( E(t) = [A + Bt^m + Ct^n]^{-1} \) and \( E(t) = \left[ bt^y + c \left( 1 - \frac{1}{1 + at^x} \right) t^z \right]^{-1} \) for PMDA-ODA and Upilex-R® films respectively. The resulting modulus master curves and fitting parameters are shown in figures 3.22 and 3.23.

3. **Viscoelastic Shrinkage Predictions**

A computer code was developed that solves the viscoelastic convolution integrals shown in equations 3.6 and 3.7 for arbitrary thermal and stress histories. This code is listed in Appendix E. The code was designed to calculate the stress and strain responses for a series of arbitrary stages with pre-specified thermal and stress histories. Once the thermal history to be imposed on the sample is specified, the reduced time, \( \xi \), is calculated by integrating over the shift function using equation 3.7. The stresses and strains for each stage are then calculated at reduced time, \( \xi \), by performing the convolution integrations over the reduced time range \( 0 \leq \zeta \leq \xi \) using a trapezoidal technique of integration.

The code was tested by performing isothermal creep and stress relaxation simulations on simple exponential constitutive equations and comparing the results to analytical solutions. The number of calculating intervals in each stage could be varied, however, calculation runs using 20 or more intervals per stage produced identical results. All results shown in this study were obtained using 50 intervals per stage. Simulations performed for PMDA-ODA and Upilex-R® films were performed using the analytical expressions for the compliance, modulus, thermal expansion coefficients and shift functions obtained in the last section.

Figures 3.24 and 3.25 show both the simulated and measured results from controlled shrinkage cycles performed on PMDA-ODA films. All heating rates and
(Figure 3.22) Modulus master curve at 30°C for PMDA-ODA polyimide film.

Fitting Function:
\[ E(t) = [A + Bt^m + Ct^n]^{-1} \]

- \( A = 2.538 \times 10^{-4} \) [MPa\(^{-1}\)]
- \( B = 9.303 \times 10^{-5} \) [MPa\(^{-1}\)s\(^m\)]
- \( C = 3.289 \times 10^{-15} \) [MPa\(^{-1}\)s\(^n\)]
- \( m = 0.05 \)
- \( n = 0.64 \)

(Figure 3.23) Modulus master curve at 30°C for Upilex-R® film.

Fitting Function:
\[ D(t) = Bt^m + C \left( 1 - \frac{1}{1 + At^k} \right) t^n \]

- \( A = 2e-6 \) [s\(^k\)]
- \( B = 3.1e-4 \) [MPa\(^{-1}\)s\(^m\)]
- \( C = 1.4e-3 \) [MPa\(^{-1}\)s\(^n\)]
- \( k = 0.23 \)
- \( m = 0.015 \)
- \( n = 0.04 \)
- \( R = 0.9995 \)
(Figure 3.24) Part (A) Strain versus temperature data for simulated and measured controlled shrinkage cycles. (0 to 1 - heating under zero stress, 1 to 2 - isostrain cooling, 2 to 3 - stress release, 3 to 7 - heating and cooling under zero stress)

Part (B) Stress results for PMDA-ODA during isostrain cooling stage during simulated and measured controlled shrinkage cycles.
(Figure 3.25) Part (A) Strain versus temperature resulting from simulated and measured controlled shrinkage cycles. (0 to 1 - heating under zero stress, 1 to 2 - isostrain cooling, 2 to 3 - stress release with 24 hr isotherm, 3 to 4 - heating under zero stress, 4 to 5 - free shrink cooling)

Part (B) Stress versus temperature during isostrain cooling of controlled shrinkage experiment

Part (C) Strain versus time during isothermal stage after stress release.
temperatures used in the simulation were identical to those used in the actual controlled shrinkage measurements performed on these materials and the responses of both materials were likewise very similar to those actually measured on the films. Both the simulated and measured results reveal a weak time dependence of stored strain at room temperature. However, the simulations predict a slightly lower amount of strain storage than actually measured. The simulations also predict a greater amount of stress development than actually measured as well. The measured and simulated responses of Upilex-R® films show very close agreement as shown in figure 3.26.

In order to observe strain storage under isothermal conditions, simulated drawing experiments similar to those shown in figures 3.10 and 3.11 were performed on PMDA-ODA samples at 30 and 240°C. The strains of up to 30% were applied at a rate of 1%/min and released at the same rate. The resulting measured and simulated stress-strain curves are shown in figures 3.27 and 3.28. The samples were then subjected to thermal cycles up to 300°C to observe shrinkage behavior. The measured and simulated shrinkage results for each temperature are shown in figures 3.29 and 3.30. The most noticeable feature in the stress-strain curves is the very large stresses needed to produce stored strains comparable to those actually measured on films drawn to only 5% strain. This indicates that linear viscoelasticity calculations do not work all that well for large strains and that a non-linear theory is probably needed in these regions. The lack of sensitivity of linear viscoelastic predictions at the higher strains may also partially account for the consistently low predictions of stored strain in the controlled shrinkage experiments shown in figures 3.24 and 3.25. However, the shortcomings of linear viscoelasticity and the large strains come as no surprise. In most cases, the amount of shrinkage observed in the materials used in this study were on the order of 1% which fall well within the applicability of linear theories. Simulated shrinkage responses showed close agreement to the measured shrinkages at each temperature.
(Figure 3.26) Part (A) Strain verses temperature data for simulated and measured controlled shrinkage cycles. (0 to 1 - heating under zero stress, 1 to 2 - isostrain cooling, 2 to 3 - stress release, 3 to 7 - heating and cooling under zero stress)

Part (B) Stress results for Upilex-R® during isostrain cooling stage during simulated and measured controlled shrinkage cycles.
Simulated and measured stress-strain curves for PMDA-ODA polyimide film stretched at low temperatures.

Simulated and measured stress-strain curves for PMDA-ODA polyimide film stretched at high temperatures.
(Figure 3.29) Simulated and measured shrinkage behavior for PMDA-ODA films stretched at low temperatures.

(Figure 3.30) Simulated and measured shrinkage behavior for PMDA-ODA films stretched at high temperatures.
4. **Cooling Rate Effects**

Although the polyimides investigated in this study show clear signs of time-dependent mechanical behavior, the development of cooling stresses in these and many other polymers are typically insensitive to cooling rate. On the surface, these two observations appear to be in conflict. However, this type of rate independence in viscoelastic materials is not uncommon and in many cases is actually predicted by viscoelastic theory. One well-known example was demonstrated by Smith where it was shown that the slope of the stress-strain curve resulting from an isothermal, constant strain rate tensile test on a linear viscoelastic material is exactly equal to the time-dependent relaxation modulus of the material but independent of strain rate.

Similar behavior can be predicted for thermally induced stresses in linear viscoelastic materials as well. Although rate effects in non-isothermal cases are not completely eliminated due to the non-linear relationship between the real and reduced times, these effects are still small. Figures 3.31 and 3.32 demonstrate the effects of cooling rate on the simulated stress development in both PMDA-ODA and Upilex-R® films for cooling rates varying between 0.001 and 1000 °C/min. In both materials, the cooling stresses are very weak functions of the cooling rate. A six order of magnitude difference in cooling rate changes the final cooling stress by about 10 MPa for PMDA-ODA and has a much smaller effect on the Upilex-R® material. For normal ranges of cooling rates these effects are difficult to observe.

**E. Summary and Conclusions**

The main goal of this study was to establish the existence of a quantitative relationship between irreversible shrinkage behavior and stress history. There were
(Figure 3.31) Calculated stress development for PMDA-ODA with different cooling rates.

(Figure 3.32) Calculated stress development for Upilex-R® with different cooling rates.
primarily two reasons for this study. The first was that knowledge of the origins of irreversible shrinkage could aid in finding ways to control this behavior. Second, irreversible shrinkage could potentially provide information about the stress history and possibly even the constitutive properties of materials.

The first part of this study demonstrated a few different aspects of shrinkage behavior and showed a qualitative relationship between shrinkage and stress history for a few different well-behaved materials. The relationship between the glass transition and cure temperature in spin coated PMDA-ODA films could be seen easily in the shrinkage behavior.

The last part of this study attempted to quantify this relationship for two different polyimides with knowledge of the material constitutive properties. It was found that linear viscoelasticity can describe all of the qualitative features of stored strain and shrinkage behavior and can give fairly accurate predictions of shrinkage for applied strains on the order of 1%. The calculations suggest that irreversible shrinkage can provide quantitative information about the stress history for polyimide films. Examples of the use of irreversible shrinkage for determining the principal directions of processing stresses in Kapton® films will be shown in the next chapter.
References


CHAPTER IV

ANALYSIS OF STRESSES ARISING DURING TENTER FRAME PROCESSING

A. Introduction

Materials such as polyethylene terephthalate (PET), polypropylene, polyimides, and other thermoplastics are often manufactured using tenter frames, that convey and draw the films through various heating and cooling processes. Two problems are often associated with films produced on tenter frames. First, the films often display in-plane orientational anisotropy. Several studies have demonstrated anisotropic behavior in the thermal expansion coefficients and moduli of commercial polyimide films with principal directions of orientation occurring at ±45° to the machine direction. Second, films produced on tenter frames also display non-uniformity in orientation behavior. Film obtained from the edges of the line typically displays greater anisotropy than film obtained from the middle. This leads to added problems of non-flatness and warping.

Anisotropy and non-uniformity have proven to be difficult problems to eliminate. This is primarily due to a lack of understanding of the stresses developed during processing. Experimental investigation of these problems is often hampered by the expense of running large lines at many different variables. Smaller pilot lines can also be relatively expensive and, as will be shown, do not always scale up appropriately. The approach taken here will be to model the stresses arising in a film on a simplified tenter frame with the idea that it is these stresses that give rise to orientational anisotropy and are largely responsible for anisotropic stored strains in the material as well. The goal of this analysis is to paint a semiquantitative picture of the processing stresses and to demonstrate how they arise. This, combined with information about the constitutive
behavior of the material it will then be possible to determine what processing variables affect the in-plane anisotropy and material properties. Methods will also be discussed on how to use the processing stresses to eliminate or at least reduce the amount of anisotropy in the final material.

In order to accomplish this goal and still keep the model relatively simple, several assumptions will be made about the material behavior and processing conditions. The main assumptions are: 1) the material obeys linear elasticity, 2) the external strains imposed on the material can be described by small strain theory, and 3) gradients in processing conditions such as temperature, and solvent concentration occur only in the machine direction. Although these assumptions place some obvious limitations on the quantitative applications of the model, the qualitative interpretation will still remain valid in many regions in the line. The limitations of the model will be discussed along with means to apply it to more general situations.

B. Experimental Characterization

Anisotropy and non-uniformity are typically revealed in both the orientation dependent properties and the irreversible shrinkage behavior displayed by the material. Since both of these phenomena are experimentally accessible, it is possible to use this information to probe the stress behavior arising during processing. This was done on two 60 inch wide sheets of 100 HN Kapton® obtained from duPont.

It was demonstrated in Chapters II and III that orientation and irreversible shrinkage originate from two separate processes during polyimide cure. As a result, orientation and shrinkage stress profiles do not necessarily need to coincide. In fact, these profiles can be useful for probing the stress conditions on the material during the different stages of processing.
1. Orientation Measurements

The directions of maximum orientation across the width of the film were obtained using an Olympus microscope in a transmission mode. The film was rotated between two cross polarizers and the transmitted light intensity was observed by eye. Rotations that produced maximum light transmission correspond to either a maximum or minimum in orientation. A film that was rotated a full 360° would give four positions of maximum light intensity at 90° intervals. Determining which positions corresponded to maximum orientations and the magnitude of the orientation was determined using a polarized helium-neon laser (\(\lambda=6328\text{Å}\)) and a Babinet compensator. Results of the orientation measurements are shown in figure 4.1 and 4.2.

2. Measurements of Shrinkage Behavior

Although the irreversible shrinkage behavior displayed by Kapton® is easily measurable with a good thermal mechanical analyzer (TMA), in order to characterize the full two-dimensional shrinkage behavior at a point across the width, a minimum of at least three TMA measurements are necessary. To characterize the behavior across the width of the line the number of measurements at each point must be multiplied by the number of points necessary to obtain a good width profile.

The magnitudes and directions of maximum shrinkage across the films were determined by a much less tedious method using time-averaged holographic interferometry developed by Maden, Tong and Farris and described in more detail in Chapter II^4.5. Steel washers (2.5 in. OD, 1.57 in. ID) were adhered to the polyimide films at various positions across the width using a high curing temperature epoxy. As the samples are heated to 300°C, the epoxy cures and stored strain energy is relaxed out of the polyimide films. As the samples cool, stresses develop in the polyimide as a result differential thermal expansion between the steel washers and polyimide films. The
(Figure 4.1) Orientation profile across Kapton® sheet (Lot #1).

(Figure 4.2) Orientation profile across Kapton® sheet (Lot #2).
magnitude and directions of principal stress should correspond to the magnitudes and directions of irreversible shrinkage.

Use of the holographic technique for residual stress measurements has been described in detail in past publications. Stressed drumlike membranes are vibrated at different frequencies under vacuum using a piezo-electric shaker. The resonant modes and frequencies of vibration are determined using a holographic interference technique that gives a visual representation of the mode of vibration as shown in figure 4.3. For a circular membrane under an isotropic state of stress, the residual stress is related to the resonant frequencies through the following relation:

\[
\sigma = 4\pi^2 \frac{\rho f_{1,n}^2 R^2}{Z_{2,n}^2}
\]

where
\[
\begin{align*}
    f_{1,n} & = \text{frequency of vibration} \\
    R & = \text{sample radius} \\
    Z_{2,n} & = \text{1th zero of the nth order Bessel Functions} \\
    \rho & = \text{sample mass density} \\
    \sigma & = \text{equibiaxial residual stress.}
\end{align*}
\]

For samples under an anisotropic state of stress it has been determined that the orientation of the various modes of vibration correspond to the principal directions of stress in the sample. Although a rigorous mathematical solution for the resonant modes and frequencies of vibration of a circular sample under an anisotropic stress state has not been found, an estimate of the relative difference between the principal stresses can be obtained by:

\[
\frac{\sigma_1 - \sigma_{II}}{\sigma_1 + \sigma_{II}} = \frac{f_{1}^2 - f_{II}^2}{f_{1}^2 + f_{II}^2}
\]
(Figure 4.3) Holography patterns for sample at edge of the line. (Taken from Lot #2 edge B)
where \( \sigma_i \) and \( f_i \) designate the principal stresses and the corresponding resonant frequencies. The results from holography measurements across the width of the two Kapton\textsuperscript{®} films are shown in figures 4.4 and 4.5.

3. Discussion

Figures 4.4 and 4.5 show large differences between orientation and shrinkage stress profiles in Kapton\textsuperscript{®} films. The birefringence profiles in figure 4.2 are almost symmetrically V-shaped giving maximum orientation at the edges with very little birefringence in the center. The angles of maximum orientation vary between ±30° to the machine direction. These features are in agreement with other past observations. On the other hand, the shrinkage stress profiles display a large amount of asymmetry across the width. On lot #1, the largest shrinkage occurs in the machine direction on one side of the line but occurs at 60 to 70° on the other side. The maximum shrinkage in lot #2 occurs -20 to -50° to the machine direction all the way across the width of the film.

C. Stress Analysis

1. What stresses exist during processing?

The full state of stress in a material is characterized by six independent components: three normal stresses and three shear stresses (figure 4.6). It can be shown that if no constraints are imposed on the surfaces of a film, stresses acting through the thickness of the film are very small compared to the in-plane stresses and can subsequently be ignored. As a result, the state of stress in a two-dimensional
(Figure 4.4) First principal direction and anisotropy for Kapton lot #1 measured by holography.

(Figure 4.5) First principal direction and anisotropy for Kapton lot #2 measured by holography.
(Figure 4.6) Components of the stress tensor.
system such as a film can be characterized sufficiently by three in-plane stresses: two normal stresses, $\sigma_{xx}$ and $\sigma_{yy}$, and one shear stress, $\sigma_{xy}$. The origin of the two normal stresses in tentering operations is fairly clear. As the film is drawn or undergoes shrinkage due to temperature changes or curing, tension would be expected to develop in the film. The origin and behavior of the shear stress are not as apparent. However, it will be shown that if any gradients are present in the line, an in-plane shear stress must exist and can be significant.

Newton's law of motion states that all forces acting on a non-accelerating body must add to zero. This also means that all stresses acting within a material must obey a force balance known as the equations of equilibrium. If body forces are ignored, the equations of equilibrium in two dimensions and in Cartesian coordinates are:

$$\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} = 0$$
$$\frac{\partial \sigma_{xy}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} = 0$$

In this case, the $x$ and $y$ directions correspond to the machine and transverse directions in the line with the $x$-axis lying halfway across the width of the line, as shown in figure 4.7. The edges of the line are therefore designated by $y = \pm W$.

If temperature and other processing conditions change only along the machine direction, then one can demonstrate that gradients in the transverse direction, $\left(\frac{\partial \sigma_{xx}}{\partial y}\right)$, can be ignored. As a result, the shear stress can be related directly to the stress gradients in the machine direction:

$$\sigma_{xy} = -\frac{\partial \sigma_{xx}}{\partial y}$$

It will be shown that the existence of a shear stress has some dramatic effects on stress anisotropy in the film. However, for now it is important to make three
(Figure 4.7) Definition of coordinate axes used in stress analysis.
observations from the relation above. First, the shear stress is directly proportional to
the normal stress gradients, \( \frac{\partial \sigma}{\partial x} \), in the line. Stress gradients arise from changes in
processing conditions such as temperature, strain, and solvent concentration, which
means that these changes are also responsible for the existence of a shear stress. One
way of looking at this problem is that the film is being pulled towards regions of high
stress. Since the edges of the film are fixed in place by the frame, material in the middle
of the line is displaced relative to the edges and shear stresses develop in the film.

Second, the shear stress varies linearly across the width of the line. Since \( y=0 \)
at the middle of the line, the shear stress must also disappear in the middle of the line.
Likewise, the magnitude of the shear stress also becomes largest at the edges of the
line. If the argument can be made that the shear stresses are largely responsible for the
stress anisotropy, then anisotropy would be expected to be greater at the edges of the
line (which is just what is found in most tenter frames). This second observation brings
up some serious consequences about the effects of line width on anisotropy in the film.
The only factors determining the magnitudes of the edge shear stresses are gradient
effects and the width of the line. Wider lines will therefore produce greater shear
stresses in the material than narrower lines experiencing the same stress gradient. This
also means that films produced on narrower lines would be expected to have fewer
problems with anisotropy than films made on wider lines.

Last, the stress behavior displayed in tentering operations is reminiscent of the
stress behavior found in many fluid flow problems such as the flow of a fluid through a
pipe or channel. In fact, no assumptions have been made about the properties of the
material up to this point, which means that shear stresses will arise in the material as a
result of stress gradients whether it is solid, fluid, or even viscoelastic.
2. Effect of Processing Conditions

In order to assess the effect of processing conditions on the state of stress, it is necessary to make several assumptions about the behavior of the material. The assumptions made here will be that the material is linearly elastic, isotropic, and homogeneous. These assumptions will obviously limit the generality of the final results; however, the limitations are not as bad as they may seem. There are usually areas in the line where the properties of the material change dramatically with position. However, there are also many regions where the material properties remain elastic in nature and reasonably constant. Although linear elasticity cannot be applied over the entire line at once, it is possible to use an incremental approximation to consider certain regions in the line separately. This means that the analysis can be applied to a single region such as a drying or cooling stage without the history of the material in previous regions.

For a linear, isotropic, homogeneous material the behavior of the stresses can be described in terms of the mechanical strains and thermal and drying effects occurring in the material. The equations of two-dimensional, isotropic linear elasticity are:

\[
\begin{align*}
\sigma_{xx} &= \frac{E}{(1 - v^2)}(\epsilon_{xx} + v\epsilon_{yy}) - \frac{E}{(1 - v)}(\alpha \Delta T + \beta \Delta c) \\
\sigma_{yy} &= \frac{E}{(1 - v^2)}(\epsilon_{yy} + v\epsilon_{xx}) - \frac{E}{(1 - v)}(\alpha \Delta T + \beta \Delta c) \\
\sigma_{xy} &= \frac{E}{(1 + v)}\epsilon_{xy}
\end{align*}
\]

where

\[
\begin{align*}
E &= \text{Tensile modulus} \\
v &= \text{Poisson's ratio} \\
\alpha &= \text{Linear thermal expansion coefficient} \\
\beta &= \text{Linear swelling expansion coefficient} \\
T &= \text{Temperature} \\
c &= \text{Solvent concentration}.
\]
The mechanical strains, $\varepsilon_{ij}$, can be described in terms of the displacements, $u$ and $v$, in the machine and transverse directions, respectively, using small-strain theory:

\[
\begin{align*}
\varepsilon_{xx} &= \frac{\partial u}{\partial x} \\
\varepsilon_{yy} &= \frac{\partial v}{\partial y} \\
\varepsilon_{xy} &= \frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)
\end{align*}
\]

In order to relate the stresses to the processing conditions it is necessary to set up and solve a boundary value problem either in terms of the stresses or the displacements. Although it is difficult to state initially what the stresses are at the boundaries, the displacement boundary conditions can be stated readily. In a tenter frame where no drawing is imposed on the film, the rails of the frame run parallel to each other and only serve to prevent the film from shrinking during processing. In this case, material at the edges of the line is held in place by the frame and the displacement boundary conditions are simply:

\[
u(y=\pm W) = 0 \quad \text{and} \quad v(y=\pm W) = 0 \quad (4.6)
\]

where $W$ is half the total width of the line.

If the equations of linear elasticity (equation 4.5) are combined with the equations of equilibrium (equation 4.3), two coupled, second-order, differential equations are obtained in terms of the displacements $u$ and $v$:

\[
\begin{align*}
\frac{\partial^2 u}{\partial x^2} + \frac{1}{2}(1-v)\frac{\partial^2 u}{\partial y^2} + \frac{1}{2}(1+v)\frac{\partial^2 v}{\partial x \partial y} &= (1+v)\left( \alpha \frac{dT}{dx} + \beta \frac{dc}{dx} \right) \\
\frac{\partial^2 v}{\partial y^2} + \frac{1}{2}(1-v)\frac{\partial^2 v}{\partial x^2} + \frac{1}{2}(1+v)\frac{\partial^2 u}{\partial x \partial y} &= 0.
\end{align*}
\]

(4.7)

If one can further assume that the processing gradients, $\frac{dT}{dx}$ and $\frac{dc}{dx}$, remain essentially constant over the given region then the solution to these equations with these boundary conditions gives:
\begin{align*}
  u &= \frac{(1+v)}{(1-v)} \left[ \alpha \left( \frac{dT}{dx} \right) + \beta \left( \frac{dc}{dx} \right) \right] (W^2 - y^2) \\
  v &= 0.
\end{align*}

This result describes the displacement profile in the film. Note that in the presence of thermal or swelling gradients a parabolic displacement profile is created across the width of the film. This profile describes how the film is pulled towards regions of high positive stress in the line and can actually be seen in some lines.

The stresses in the system can be found by substituting the result above (equation 4.8) into the equations of elasticity (equation 4.5):

\begin{align*}
  \sigma_{xx} &= \sigma_{yy} = -\frac{E}{(1-v)} (\alpha \Delta T + \beta \Delta c) \\
  \sigma_{xy} &= \frac{E}{(1-v)} \left[ \alpha \left( \frac{dT}{dx} \right) + \beta \left( \frac{dc}{dx} \right) \right] y.
\end{align*}

This result points out several characteristics about the state of stress tenter frames. First, as noted earlier, the shear stress is directly proportional to the transverse position, \( y \), in the line. Second, the shear stress is independent of temperature and solvent concentration but is proportional to their gradients. This means that the distance over which a material is cooled or dried determines the amount of shear stress in the line. Cooling or drying a material over a short distance creates large gradients in the line and hence will produce large shear stresses as well. Last, in the absence of externally applied strains (drawing), the two normal stresses are equal. This is important since it also means that in this case anisotropy in the material is brought about only by the presence of the shear stress. How the shear stress affects anisotropy will be discussed next.
3. **Stress Anisotropy**

Like all tensors, the state of stress in a material is independent of direction. However, how it is perceived through its components depends on the coordinate system chosen to describe it. For any tensor it is possible to find a unique coordinate system where all shear components disappear and the magnitude of the tensor is expressed in terms of only its normal (principal) components acting along the axes of the new coordinate system. The directions in which these stresses act are known as the principal directions. This means that for a completely general two-dimensional system, it is possible to describe the state of stress in terms of two perpendicular normal stresses and their directions.

Since the goal of this analysis is to describe how tentering processes affect the state of orientation in materials, the principal stresses and directions provide a convenient means of relating the state of stress in the material to orientation measures found from methods such as birefringence and dichroism techniques commonly used to characterize polymeric films. Whereas it is difficult for most people to develop any intuitive picture of how three separate stresses can affect orientation in a material, it is much easier to understand how two perpendicular stresses can affect this orientation. The question now is: How does one express three independent stresses in terms of two normal stresses and a direction?

If one consults any introductory text on continuum mechanics such as Malvern's *Introduction to the Mechanics of a Continuous Medium* or Timoshenko and Goodier's *Theory of Elasticity*, one will find that the state of stress or strain in a material can be described in terms of a plot known as Mohr's Circle\(^6\).\(^7\). If the shear stress at a point and in a given direction is plotted against the normal stress at the same point and direction for all possible rotations of the coordinate system chosen to describe the direction, the result is a circle with a center lying at \(\frac{1}{2}(\sigma_1 + \sigma_{||}), 0\) where \(\sigma_1\) and \(\sigma_{||}\) are the principal stresses at the point. The locations where the circle intersects the normal stress...
give the individual values for the principal stresses (σI and σII). This is shown in figure 4.8.

The selection of the coordinate axes in the system one wishes to describe determines the position on Mohr's circle. For instance, in the case of a film on a tenter frame it is most convenient to choose a Cartesian coordinate system with x and y-axes lying parallel to the machine and transverse directions, respectively. If the principal directions do not lie in the machine or transverse directions, then the stress tensor will have a shear component, σxy, and two normal components, σxx and σyy, that will give the points (σxx, σxy) and (σyy, -σxy) on Mohr's circle, as shown in figure 4.8. The principal directions can be found by taking half of the rotation, θ, necessary to travel between the point (σxx, σxy) or (σxx, -σxy) and the normal stress axis.

The principal stresses and directions can also be expressed algebraically in terms of the stress components, σxx, σyy and σxy in the xyz-coordinate system:

\[
\sigma_n = \frac{1}{2} (\sigma_{xx} + \sigma_{yy}) \pm \sqrt{\frac{1}{4} (\sigma_{xx} - \sigma_{yy})^2 + \sigma_{xy}^2}
\]

\[
\theta_n = \pm \frac{1}{2} \arctan \left( \frac{2\sigma_{xy}}{\sigma_{xx} - \sigma_{yy}} \right) \quad n = I \text{ or II}
\]

(4.10)

where σn are the principal stresses and θn are the angles between the principal directions and the coordinate axes. If both stresses are equal one would not expect to find any preferred orientation in the material. However, if the two stresses are different from one another, one would expect to find preferred orientation within the plane of the film in the direction of the largest principal stress.

Instead of using the two principal stresses to characterize orientation, a value based on the relative difference between the principal stresses will be used, which we will call the anisotropy, A:

\[
A = \frac{|\sigma_I - \sigma_{II}|}{|\sigma_I + \sigma_{II}|}.
\]

(4.11)
(Figure 4.8) Mohr's circle for two-dimensional stress state.
For a completely isotropic state of stress the two principal stresses are equal and therefore $A$ must be zero. As $A$ gets larger the relative difference between the principal stresses becomes larger, and one would expect a greater influence on stress anisotropy within the film. Note that an anisotropy, $A$, greater than unity indicates that one of the principal stresses is in compression. Since free-standing films do not support compression, $A$ is useful only when it is less than unity.

It was found earlier that in the absence of external drawing the two normal stresses in the machine and transverse directions were equal. This will have two effects on orientation. The first effect is on the direction of orientation. From Mohr's circle and equation 4.10 it can be shown that if the two normal stresses are equal then the principal directions must lie at $\pm 45^\circ$ to the machine direction. If one measures the direction of maximum orientation at each point across the full width of a film taken from a tenter frame, the orientation profile would be expected to look like that shown in figure 4.9. This means that in the absence of external drawing the tenter frame tends to stretch the film at angles $\pm 45^\circ$ to the machine directions, which explains the orientation behavior found in the literature for commercial Kapton®.

The second effect of equal normal stresses is on the degree of anisotropy. If one sets $\sigma_{xx}$ and $\sigma_{yy}$ equal in equation 4.10, one finds that the anisotropy is directly proportional to the shear stress:

$$A = \frac{\left|\sigma_{xy}\right|}{\sigma_{xx}}. \quad (4.12)$$

This means that in the absence of external drawing the shear stress and hence the stress gradients give rise to the anisotropy in the line. A similar conclusion was also reached in an analysis of biaxially drawn films by Jungnickel. The amount of anisotropy can be controlled directly by changing the stress gradients in the line.
(Figure 4.9) Orientation profile in cooling section of a polyimide tenter frame.
In order to better visualize the effects of stress gradients on anisotropy it is helpful to consider an example. The cooling region in polyimide processing is ideally suited for the application of this analysis since the material properties of polyimides are elastic and reasonably constant over very large temperature ranges. During the cooling of a polyimide line the material may see changes in temperature greater than 300°C. If one uses a typical polyimide modulus 3 GPa, a Poisson's ratio of 0.35, a thermal expansion coefficient of 30 ppm/°C and a cooling distance of 5 meters one finds that, upon cooling, the polyimide film is under a biaxial stress of about 40 MPa. The resulting shear stress at the edges of a 2 meter wide line would be about 8 MPa. A plot of how these stresses develop is shown in figure 4.10.

During the initial stages of cooling where temperatures are high and the normal stresses are low, the shear stress will dominate at the edges producing a distinct V-shaped anisotropy profile across the width of the line. This is shown in figure 4.11. As the material cools, the biaxial stresses begin to dominate, causing the V-shaped profile to flatten out. This indicates a more uniform and less anisotropic state of stress in the material. As mentioned previously, an anisotropy greater than one indicates that one of the principal stresses is in compression. Since thin films cannot support compressive stresses, this could result in buckled regions at the edges in the early cooling stages.

In many tentering operations it is possible to see displacement profiles across the film. Material in the center of the line is displaced with respect to the edges, creating a bowed displacement profile in the direction of the stress gradient. This calculated profile is described by \( u \), the displacement in the machine direction, and is shown for the example above in figure 4.12. This plot shows that under the cooling conditions discussed in this example, material in the center of the line is displaced 3.7 mm forward with respect to the edges. It should be noted that a 3.7 mm displacement over a 2 meter wide line creates only a small strain in the material and as a result would not be expected to have a large effect on orientation. This observation indicates that although very large
Resulting normal and shear stresses resulting from cooling a 2 m wide polyimide line 300°C over a distance of 5 m.

Anisotropy profile in cooling section of a polyimide tenter frame.
(Figure 4.12) Calculated displacement profile resulting from cooling section of tenter frame.
and anisotropic stresses exist in the material during cooling, most of the actual
deformation and orientation development in the material probably take place earlier in
the process, as would be expected. The cooling stresses can, however, affect strain
storage in the material and in turn affect the irreversible shrinkage upon later heating.

It should also be noted that in some cases, such as the tentering of PET films,
the displacement profiles are observed to occur in the negative direction. This indicates
that material in the middle of the line has been pulled backward with respect to the
edges. These cases are rather special and indicate that the profiles were frozen into the
material in a region in the line where the stress gradient was negative.

In summary, it was found that using linear elasticity and the equations of
equilibrium one can predict that the principal directions of stress lie at ±45° to the
machine direction and that the magnitude of the anisotropy in tenter frames arises from
stress gradients in the line. Stress gradients in turn arise from processing gradients such
as changes in temperature or solvent concentration. The anisotropy increases linearly
from the center of the line, reaching a maximum at the edges. As a result, wider lines
would be expected to have greater anisotropy than narrower lines.

D. Extensions to the Model

The analysis presented so far has been derived for a very limited case. However,
the general concepts such as the influence of stress gradients and shear stress apply to a
wide variety of cases. Many of the orientation and shrinkage profiles measured on
tentered films display behavior not predicted by the analysis performed so far. A few
extensions to the model will be presented here to give some possible causes for different
profiles.
1. The Effects of Drawing

In many instances the directions of orientation observed in processed films do not lie along the $45^\circ$ as predicted from thermal or drying stresses alone. This indicates that the stress in the line is dependent on other conditions in addition to thermal and drying effects. During most tentering operations, external strains are usually imposed through machine and transverse drawing of the material. The effects of drawing can be taken into consideration simply by changing the boundary conditions for the displacements at the edges of the line. These will be used as before to solve the two coupled differential equations (equation 4.7) to obtain the displacement profiles in the line.

The boundary conditions in the case of film drawing can best be described in terms of the strains, $\varepsilon_{xx}$ and $\varepsilon_{yy}$, at the edges of the line. Transverse drawing is accomplished by forcing the rails of the frame to diverge as they travel down the line. Machine direction drawing is often accomplished either by placing several processing steps in series and/or accelerating the clips in the tenter. One can consider two types of strain: initial strains arising in the material from previous processing stages and strains arising from drawing imposed on the film while in the region being analyzed. The overall strains can be expressed:

$$
\begin{align*}
\varepsilon_{xx}(y=\pm W) & = \varepsilon_{xx0} + k_x x \\
\varepsilon_{yy}(y=\pm W) & = \varepsilon_{yy0} \pm k_y x
\end{align*}
\tag{4.13}
$$

where $\varepsilon_{xx0}$ and $\varepsilon_{yy0}$ are the terms representing the initial strains in the film and $k_x$ and $k_y$ are the strain gradients or the terms describing how fast the material is being drawn. The strain gradients can also be expressed in terms of the change in strain imposed on the material over a given distance:

$$
k_x = \left( \frac{\partial \varepsilon_{xx}}{\partial x} \right)_{y=\pm W}
$$
\[ k_y = \left( \frac{\partial \varepsilon_{xx}}{\partial x} \right)_{y=\pm W}. \]

Using small-strain theory one can express the boundary conditions in terms of the displacements by integrating the two parts to equation 4.13 with respect to \( x \) and \( y \):

\[
\begin{align*}
u(y=\pm W) &= \varepsilon_{yy0} W \pm k_y W \\
v'(y=\pm W) &= \varepsilon_{yy0} W \pm k_y W.
\end{align*}
\]

Solving for the stress in the manner used earlier one finds:

\[
\begin{align*}
\sigma_{xx} &= \frac{E}{(1-v)} \left( \frac{\varepsilon_{xx0} + \nu \varepsilon_{yy0}}{(1+v)} \frac{(k_x + nk_y)}{(1+v)} x - \alpha \Delta T - \beta \Delta c \right) \\
\sigma_{yy} &= \frac{E}{(1-v)} \left( \frac{\varepsilon_{yy0} + \nu \varepsilon_{xx0}}{(1+v)} \frac{(k_y + nk_x)}{(1+v)} x - \alpha \Delta T - \beta \Delta c \right) \\
\sigma_{xy} &= \frac{E}{(1-v)} \left( \frac{(k_y + nk_x)}{(1+v)} - \alpha \frac{\partial T}{\partial x} - \beta \frac{\partial c}{\partial x} \right) y.
\end{align*}
\]

This result shows that in general, stresses in a linear elastic material arise from two additive sources: changes in the thermal and drying conditions and external strains. The effects of external strains on the shear and normal stresses are also analogous to the effects found earlier from changes in temperature and solvent content. While the normal stresses depend on the absolute strains imposed on the material, the shear stress arises from gradients in the external strains or how much they change over a given distance.

When external strains are imposed on the material, the two normal stresses are no longer always equal. This means the principal directions do not always lie at \( \pm 45^\circ \) to the machine direction but can vary depending on the magnitude of the strains imposed on the material and how they are applied. These effects can be seen by reconsidering the example of the polyimide line discussed earlier.

Although the state of stress in polyimide coatings is usually zero at the highest curing temperature, this is not necessarily true for films processed on tenter frames. If one considers a situation where a 1% strain (\( \varepsilon_{xx0} = 0.01 \)) has been imposed on the
polyimide film in the machine direction before entering the cooling region, very
different orientation and anisotropy profiles result, as shown in figures 4.13A and B.
The first principal stress is no longer oriented at only ±45° but has been rotated towards
the machine direction. Also, the anisotropy profile is no longer V-shaped but has
become more parabolic in nature because of the lack of isotropy in the middle of the
line.

One can consider the effects of gradual drawing on the orientation and
anisotropy by allowing the rails of the line in this example to diverge enough to produce
an additional 1% transverse strain in the material over the entire cooling distance of 5
meters \((k_y = 0.002 \text{m}^{-1})\). The orientation and anisotropy profiles for this case are shown
in figures 4.14A and B. In the early stages of cooling, the largest principal stress lies
closer to the machine direction. As the strains in the machine and transverse directions
become equal the principal directions rotate back to ±45° to the machine direction in the
later stages of cooling. The anisotropy also transforms from the parabolic shaped
profile back to the V-shaped profile found earlier when only thermal effects were
considered.

2. Non-Symmetrical Processing Conditions

Keeping precise control over processing conditions is often difficult in practice.
As was observed in the shrinkage stress profiles, a certain amount of asymmetry can
exist in the line that may be caused by any number of reasons. The influence of two
factors will be discussed here: transverse temperature gradients and rail offsets.

The effects of transverse temperature gradients can be considered by defining
\(\Delta T\) change as being the sum of two linear functions of \(x\) and \(y\):

\[
\Delta T = \left( \frac{\partial T}{\partial x} \right) x + \left( \frac{\partial T}{\partial y} \right) y. \tag{4.16}
\]
(Figure 4.13) Part (A) Orientation profile in cooling section of a polyimide tenter frame with 1\% initial MD strain.
Part (B) Anisotropy profile in cooling section of a polyimide tenter frame with 1\% initial MD strain.
(Figure 4.14) Part (A) Orientation profiles for cooling region in polyimide line with 1% initial strain in the machine direction plus 0.002 m⁻¹ transverse strain gradient.

Part (B) Anisotropy profiles for cooling region in polyimide line with 1% initial strain in the machine direction plus 0.002 m⁻¹ transverse strain gradient.
As before, the two temperature gradients are assumed to be constant. The stresses can be found in the same manner described earlier. The resulting expressions for the stresses are:

\[
\begin{align*}
\sigma_{xx} &= \frac{\alpha E}{(1 - \nu)} \frac{dT}{dx} x - \alpha E \frac{dT}{dy} y \\
\sigma_{yy} &= \frac{\alpha E}{(1 - \nu)} \frac{dT}{dx} x \\
\sigma_{xy} &= \frac{\alpha E}{(1 - \nu)} \frac{dT}{dy} y \tag{4.17}
\end{align*}
\]

Only one term is added to the expression for \(\sigma_{xx}\) as a result of the transverse gradient. The other two stresses remain unaffected.

Transverse gradients appear to have a large effect on the principal directions of stress in the line. In equation 4.10 the principal directions were related to the processing stresses through the relation:

\[
\theta_n = \pm \frac{1}{2} \arctan \left( \frac{2\sigma_{xy}}{\sigma_{xx} - \sigma_{yy}} \right) \tag{4.18}
\]

where \(n=I\) or \(II\). The first example discussed only considered effects from thermal and solvent gradients along the machine direction, and as a result, \(\sigma_{xx} = \sigma_{yy}\). Since the difference between these terms is in the denominator of equation 4.18, the argument for the arctangent takes on values of \(\pm \infty\) depending on position across the width. This resulted in principal directions occurring at \(-45^\circ\) on one side of the line and \(+45^\circ\) on the other.

When transverse gradients are considered, the arctangent argument is proportional to the ratio between the machine and transverse gradients:

\[
\theta_n = \pm \frac{1}{2} \arctan \left( \frac{-2 \frac{dT}{dx}}{\frac{dT}{dy}} \right) \tag{4.19}
\]
Since both gradients are constant everywhere in the line, the principal directions of stress should be constant as well. In addition, temperature gradients in the machine direction are typically much larger than gradients across the width. As a result, the direction of the largest principal stress should lie at -45° for most cases and approach zero as transverse temperature gradients become larger with respect to the machine direction temperature gradient. One surprising feature of this result is that the transverse gradient only needs to be finite to force the principal directions to -45° all the way across the width of the line.

Transverse gradients appear to have only a minor effect on the anisotropy. If the stress expressions in equation 4.17 and the expression for the principal stresses (equation 4.10) are substituted into the definition of the anisotropy, A, in equation 4.11, the result is:

$$A = \frac{y\sqrt{(1-v^2)(dT/dy)^2 + 4(dT/dx)^2}}{(1-v^2)(dT/dy) y + (dT/dx)x}. \quad (4.20)$$

Small changes in the transverse gradient have only minimal effects on the anisotropy profile.

Figures 4.15A and B show the effects of a 5°C differential across the width of the line on the orientation and anisotropy. Although transverse gradients have very little effect on the anisotropy profile, the orientation profile has been forced to -45° all the way across the width. This behavior is very similar to that observed in shrinkage stress profiles measured on sheets Kapton® film (figures 4.4 and 4.5).

Further calculations revealed that similar behavior could be seen from skew effects imposed by the line. Rail offsets will occur if one rail travels a slightly longer distance than the other. This can occur as a result of slightly different velocities between the two rails or from the stretching of driving chains that may occur with time.
(Figure 4.15) Part (A) Orientation profile in cooling section of a polyimide tenter frame with 5°C temperature differential across width.
Part (B) Anisotropy profile in cooling section of a polyimide tenter frame with 5°C temperature differential across width.
It was found that a rail offset of only 20 \( \mu \text{m} \) could produce orientation and anisotropy profiles very similar to those shown in figures 4.15A and B.

Although the orientation profile is extremely sensitive to transverse gradient effects, it was found that the effects of transverse gradients are in turn extremely sensitive to external strains imposed by the frame. Figure 5.16 shows the effects of imposing small differences in the machine and transverse stresses on the previous example. It was found that a difference of only 0.3 MPa between the machine and transverse stresses was enough to eliminate the transverse gradient effects.

The sensitivity of the transverse gradients effects to drawing suggests that these effects would not be seen in the initial processing stages of tentering. Since orientation is mostly developed in the early processing stages where drawing and solvent removal occurs one would not expect to see large transverse gradient effects in orientation profiles. However, external strains are not usually imposed on films intentionally during cooling. As a result, it is highly possible for transverse gradient effects to be seen in these regions.

**E. Eliminating Anisotropy**

From the analysis so far it has been determined that stress gradients can arise from a number of sources: processing gradients due to changes in temperature and solvent content and strain gradients due to in-line drawing by the tenter frame. Although control over the processing gradients is sometimes limited, the external strains can be controlled more easily. This section will deal with how external strains may be used to counteract the effects of processing gradients to create an isotropic state of stress in the material during processing.
(Figure 4.16) Orientation profile in cooling section of a polyimide tenter frame with 5°C differential and various differences between MD and TD stresses. \( n = \text{MDstress} - \text{TDstress} \)
From Mohr’s Circle it was shown that the anisotropy can be related directly to the shear and normal stresses in the material. The algebraic form of this relation is:

\[
A = \frac{\sqrt{(\sigma_{xx} - \sigma_{xy})^2 + 4\sigma_{xy}^2}}{\sigma_{xx} + \sigma_{yy}}.\]  \tag{4.21}

To produce an isotropic state of stress during processing, one simply needs to make \(A=0\) everywhere in the line. There are two ways in which the anisotropy can become zero: when the numerator in equation 4.21 becomes zero or when the denominator becomes very large compared to the numerator.

In order for the numerator to become zero, the two normal stresses must be equal and the shear stress must be zero. If one wants the two normal stresses to be equal then one must apply equal strains in the machine and transverse directions. This means that \(\varepsilon_{xx0} = \varepsilon_{yy0}\) and \(k_x = k_y\). The shear stress can be eliminated by using the strain gradients to cancel out the effects of processing gradients on the shear stress. In other words, let the strain and processing gradients be equal, as shown below:

\[
k_x = k_y = \frac{\partial T}{\partial x} + \frac{\beta}{\partial x}.\]  \tag{4.22}

During cooling or drying, the processing gradients are negative, indicating that the strain gradients must also be negative to eliminate the shear stress. In other words, the film must be allowed to shrink during cooling to eliminate the shear stress and thus make \(\sigma_{xx}\) and \(\sigma_{yy}\) equal and constant down the length of the line. Figure 4.17 shows the resulting anisotropy profile from allowing the strain gradients to cancel the thermal effects (\(k_x = k_y = -0.0018 \text{ m}^{-1}\)) in the cooling polyimide line. By allowing the rails of the line to converge and the clip spacing to decrease at a similar rate, the stress anisotropy during cooling is completely eliminated.
(Figure 4.17) Anisotropy profile for cooling region in polyimide line where strain gradients are used to exactly cancel effects from thermal gradients ($k_x = k_y = -0.0018 \text{ m}^3$).
Balancing strain and processing gradients eliminates anisotropy by removing stress gradients in the line. The problem with using this approach is that allowing the material in the frame to expand or contract as it desires does not allow one to biaxially orient the film, which is often a major benefit for using tenter frames in the first place. Another approach to removing anisotropy is to simply mask the shear stress effects by imposing large normal stresses on the material. Although anisotropy is not completely eliminated with this approach, it can be reduced significantly while still allowing the material to be biaxially oriented by the tenter frame.

In figure 4.8 it was demonstrated that anisotropy is related to the relative magnitude of the shear stress to the normal stresses. The greatest anisotropy occurred in the initial stages of cooling where the normal stresses were small in relation to the shear stress. In order to make the normal stresses larger in the initial stages of cooling one must have a drawing stage prior to the cooling region. For our polyimide a 1% initial biaxial strain ($\varepsilon_{xx0} = \varepsilon_{yy0} = 0.01$) will create an initial biaxial stress of about 46 MPa in the film. The resulting effects on anisotropy during cooling are shown in figure 4.18. Although the anisotropy is not completely eliminated during cooling, it is reduced to a point where the two principal stresses differ at most by about 10%.

The main problem with a predrawing approach is that predrawing in itself creates shear stresses in the material through the effects of strain gradients. This means that although this approach can reduce stress anisotropy in regions where processing gradients exist, such as cooling or drying stages, it does so at the cost of creating anisotropic stresses in the predrawing regions. The value of this approach is that it allows one to greatly reduce stress anisotropy in regions critical to orientation and residual stress development at the cost of creating anisotropic stresses in possibly less important processing regions.
(Figure 4.18) Anisotropy profile for cooling region in polyimide line where a predrawing stage has been used to impose 1% initial strains in both the machine and transverse directions.
The most important point uncovered in this analysis is that in-plane shear stresses in tenter frames are a direct result of stress gradients in the line. It was also shown that the shear stress must be zero in the middle of the line and maximum at the edges, indicating that the maximum anisotropy in the material is a direct function of the line width. These two results are the underlying theme to the entire analysis and were shown to be true regardless of the behavior of the material as long as the normal stresses and processing conditions vary only in the machine direction.

In order to determine the origin of the stress gradients and make more quantitative predictions of the anisotropy profiles it was necessary to make some assumptions about the behavior of the material. Linear elasticity was chosen to describe the material primarily because of its relative simplicity. From this it was determined that stress gradients may arise from processing gradients resulting from changes in conditions such as temperature and solvent concentration and from strain gradients resulting from drawing effects. However, in order to use linear elasticity to describe the material, the properties of the material must remain constant with position in order to satisfy the homogeneity requirement.

In reality there can also be a third source of stress gradients not addressed in this analysis. Stress gradients may also arise from radical changes in thermal or mechanical properties, that often occur during phase transitions such as vitrification or crystallization. Although a quantitative prediction of these effects is difficult to obtain from this analysis as it stands, a rough description of the processing stresses can be obtained from any number of stress verses temperature measurement techniques. One commonly used technique simulating the effect of tentering on materials is biaxially stretching the material at different temperatures. Biaxial stretchers alone cannot be used to simulate the orientation profiles found in tenter frames since they do not impose
stress gradients in the material. However, they can be used for measuring changes in stress at different temperatures and drawing conditions. If the temperature and drawing conditions are known at each point in the line, then it should be possible to approximate the stress gradients and determine the state of stress in the line, even in regions where radical changes in material properties occur.
References


CHAPTER V

FORMATION AND CHARACTERIZATION OF HIGHLY CRYSTALLINE PMDA-ODA POLYIMIDES

A. Introduction

Aromatic polyimides generally have stiff, planar chemical structures that would ordinarily give rise to highly crystalline materials. However, most aromatic polyimides exhibit only limited crystallinity. Brekner and Feger reported the formation of a highly crystalline powder precipitate during the imidization of a monomeric model compound based on pyromellitic dianhydride and aniline\(^1\). However, extensive crystallinity has not been observed in polymeric aromatic polyimides. The main reason for the low crystallinity is usually attributed to a lack of chain mobility\(^2\). Polyimides originate from disordered, soluble polyamic acid precursors and usually form after solvent removal when the materials have very high viscosities. Although crystallinity in polyimides is affected by factors such as orientation, curing conditions, thickness and swelling, extensive long range order in aromatic polyimides is only observed in oriented fibers.

During the studies on gelation described in Chapter II, two forms of PMDA-ODA polyimide were found which exhibit densities significantly higher than those typically observed for this material. Polyimide powders and films were obtained from a high pressure process designed to force imidization to take place prior to solvent removal. These polyimides show signs of being potentially useful as model compounds for the characterization of crystallinity and structure property relationships in polyimide materials. This study will present a preliminary characterization of curing techniques and physical properties of these materials.
B. Experimental

1. Curing Techniques

All starting materials used in this study have been described previously in the experimental section of Chapter II. The techniques of forming chemically cured polyimide gel films have also been described therein. Curing at high pressure conditions was performed in a pressure vessel capable of sustaining pressures up to 650 psi at temperatures up to 260°C. The vessel, shown in figure 5.1, was made from three 6.25 inch diameter stainless steel vacuum flanges sandwiched with 10 steel bolts around two ethylene-propylene rubber O-rings. Two Swaglok® connections were placed in the top flange for a pressurizing inlet and a pressure relief valve. Nitrogen gas was used as a means of pressurizing the vessel and the entire vessel was small enough to be placed in a convection oven to be heated. The curing temperatures used in this study varied between 120 and 200°C and a pressure of 200 psi was used in all cases. The 200 psi pressure was chosen to ensure suppression of the dimethylacetamide (DMAc) boiling point to temperatures in excess of 200°C.

2. Optical Microscopy

Optical microscopy was performed on an Olympus PM-10AD optical microscope.

3. X-ray Measurements

Wide angle x-ray diffraction (WAXD) patterns were obtained using a Kratky camera with a sample distance of 75.2 mm and a radiation wavelength of 1.542 Å. The
(Figure 5.1) Photograph of pressure vessel.
sample distance was calibrated using a calcium carbonate reference. Powder samples were exposed for 4 hours while chemically cured films were exposed for 6.25 hours.

4. **Density**

Two techniques were used to obtain density measurements. The densities of films were found using a floatation technique. Films were submerged in a miscible mixture of carbon tetrachloride and p-xylene inside a 50 ml graduated cylinder. Various amounts of either solvent were added until films became buoyant in the solution. The density of the solvent mixture was then measured by carefully weighing 20 ml quantities at 25°C.

The density of powder material was estimated using a 1.2 ml picnometer bottle calibrated with distilled water at 25°C. The dry bottle was filled with 0.4 to 0.6 g of powder. The bottle was then filled halfway with distilled water and placed in a sonicator at room temperature for 24 hours to eliminate trapped air bubbles. The bottle was then filled to capacity with distilled water and weighed at 25°C. The mass of the bottle, powder and water was compared to the bottle filled with water only to obtain the mass of displaced water. The powder volume could then be obtained by dividing the mass of displaced water by the tabulate density of water at 25°C (0.99705 g/cm³). Density values using this technique varied by ±0.01g/cm³.

5. **Thermal Analysis**

Differential scanning calorimetry (DSC) and thermal gravametric analysis (TGA) were performed on a TA Instruments 2910 DSC and 2950 TGA. DSC measurements were carried out over a temperature range between 300 and 620°C. Samples were
contained in hermetically sealed aluminum pans and all thermal analysis runs were
performed under a nitrogen purge at a heating rate of 20°C/min.

6. Intrinsic Viscosity

Polyamic acid solutions with concentrations varying between 0.1 and 1.0 g/dl
were made from a 20 wt% stock solution of PMDA-ODA polyamic acid in
dimethylacetamide (DMAc) obtained from duPont. To reduce polyelectroli
tic effects from acid groups, 0.1 N LiBr was added to the solutions as described by Wallach.
Intrinsic viscosities were obtained using the standard techniques. The viscosities of the
various polyamic acid solutions were made using a size No. 1 Ubbelohde viscometer to
keep flow times between 100 and 600 seconds. The relative, \( \eta_r \), and specific, \( \eta_{sp} \),
viscosities are given by \( \eta_r = \eta/\eta_0 \) and \( \eta_{sp} = \eta/\eta_0 - 1 \) where \( \eta \) and \( \eta_0 \) are the viscosities
for the polymer solution and pure solvent respectively. The inherent and reduced
viscosities, \( \eta_{inh} \) and \( \eta_{red} \) are defined as: \( \eta_{inh} = \ln(\eta_r)/c \) and \( \eta_{red} = \eta_{sp}/c \) where \( c \) is the
solution concentration in units of g/dl.

The intrinsic viscosity was taken as the limit of \( \eta_{inh} \) and \( \eta_{red} \) as \( c \) approached
zero. The intrinsic viscosities of PMDA-ODA polyimides were obtained using a
technique described by Wallach. Polyimides were dissolved in concentrated sulfuric
acid to make solutions with concentrations between 0.5 and 1.0 g/dl. Viscosities for the
polyimide solutions were measured using a size No. 2 Ubbelohde viscometer. Since
sulfuric acid also degrades polyimide, Wallach suggests that intrinsic viscosities be
measured as a function of time after dissolution and extrapolated to zero time to find an
estimate of the true intrinsic viscosity.
C. Results

1. Effects of Curing

A small test tube with 5 ml of the 15 wt% polyamic acid solution was placed in the pressure vessel, subjected to a pressure of 200 psi under nitrogen, then heated to 200°C. Approximately one hour was required to reach 200°C from room temperature and the vessel was held at 200°C for another hour before cooling. During heating, the pressure increased to approximately 250 psi at 200°C. Cooling to room temperature took place over the course of two hours. Upon releasing the pressure, a bright orange slurry was obtained. When dried at 300°C under vacuum, the slurry formed a very fine bright orange powder. Curing at 170°C also produced powder, however, curing temperatures of 140°C and lower resulted in the polyamic acid solution with a visibly lower viscosity.

Chemically cured polyimide gels were also cured at 200°C and 200 psi. Acetic anhydride and 3-picoline curing agents were mixed into the polyamic acid solution and centrifuged for one minute. Five ml of the solution were placed in a small test tube and cured in the pressure vessel at 200°C and 200 psi. When a 1:1 molar ratio of 3-picoline and acetic anhydride to polyamic acid active groups was used, a dark brown slurry was obtained that upon drying formed a coarse, reddish brown powder. When a 2:1 molar ratio of curing agents was used, a solid, dark brown gel conforming to the shape of the test tube was made that remained intact upon drying at 300°C under vacuum.

A number of attempts were made to produce films using the high pressure technique. The polyamic acid and curing agent mixture was blade coated onto a 2.5 inch diameter steel substrate just after centrifugation. After the coating gelled at room temperature, the film was cured in the pressure vessel at 200°C and 200 psi. During cure, films made with a 2:1 ratio of curing agents had delaminated from the substrate and cracked into several pieces with average diameters around 5 mm. Films made with
a 3:1 ratio of curing agents remained in tact during cure but delaminated from the substrate and shrank to about 70% of their original in-plane dimensions. The swollen, dark orange gel films were brittle and had a leathery texture. Upon drying at 300°C under vacuum, the intact film shrank to about 50% of its original in-plane dimensions forming a brittle dark orange film. The film was capable of being drawn up to 50% at temperatures above 300°C.

Attempts to constrain gel films during cure by clamping them between 2.5 inch diameter steel washers or between a washer and steel substrate only resulted in cracked films. In one case, an intact film was obtained directly out of the vessel. However, upon drying in air at room temperature, the film cracked into several pieces as before. Changing curing temperatures between 100 and 200°C had no effect on cracking.

To observe the effects of pressure, heat and solvent on fully cured polyimide films, 500 HN Kapton® was placed in a small dish of DMAc inside the pressure vessel and heated to 200°C under a pressure of 200 psi. No visible changes were observed in the films after treatment. Table 5.1 summarizes the materials obtained for the various curing conditions.

2. Optical Characterization

Optical microscopy at a magnification of 1200x revealed that the powder originating from the straight polyamic acid solution consisted of spherical particles approximately 2 to 4 μm in diameter. An optical micrograph of the powder is shown in figure 5.2. The powder particles demonstrated birefringence under cross polarizers as shown in figure 5.3. Optical microscopy on the dark brown powder obtained from the chemically cured gel revealed cracked irregularly shaped particles with sizes varying between 1 and 20 μm. The chemically cured powder was also birefringent.
(Table 5.1) Summary of materials resulting from various high pressure curing conditions.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Starting Material</th>
<th>Curing Conditions</th>
<th>Resulting Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15 wt% Polyamic in DMAc</td>
<td>200 psi, 200°C for 1 hour</td>
<td>Fine bright orange powder</td>
</tr>
<tr>
<td>2</td>
<td>15 wt% Polyamic in DMAc</td>
<td>200 psi, 170°C for 1 hour</td>
<td>Fine bright orange powder</td>
</tr>
<tr>
<td>3</td>
<td>15 wt% Polyamic in DMAc</td>
<td>200 psi, 140°C for 1 hour</td>
<td>Low viscosity polyamic acid</td>
</tr>
<tr>
<td>4</td>
<td>Polyimide gel from 1:1 ratio curing agents</td>
<td>200 psi, 200°C for 1 hour</td>
<td>Coarse dark brown powder</td>
</tr>
<tr>
<td>5</td>
<td>Polyimide gel from 2:1 ratio curing agents</td>
<td>200 psi, 200°C for 1 hour</td>
<td>Cracked film</td>
</tr>
<tr>
<td>6</td>
<td>Polyimide gel from 3:1 ratio curing agents</td>
<td>200 psi, 200°C for 1 hour</td>
<td>Brittle film drawable above 300°C</td>
</tr>
<tr>
<td>7</td>
<td>500 HN Kapton®</td>
<td>200 psi, 200°C for 1 hour</td>
<td>No visible changes</td>
</tr>
</tbody>
</table>
(Figure 5.2) Optical micrograph of polyimide powder originating from straight polyamic acid solution.

(Figure 5.3) Optical micrograph under cross polarizers of polyimide powder originating from straight polyamic acid solution.
3. **X-Ray Diffraction and Crystallinity Characterization**

Wide angle x-ray diffraction (WAXD) patterns obtained for the polyimide orange powder cured at 200°C revealed a highly ordered structure as shown in figure 5.4. The d-spacings for the orange powder are listed in table 5.2. The chemically cured polyimide film was capable of being drawn up to 50% at temperatures above 300°C. A WAXD pattern obtained for the drawn film is shown in figure 5.5. The elongation imposed on this film was sufficient to separate the x-ray reflections into the meridional and equatorial components. The d-spacings for the drawn film are listed in table 5.3. It was possible to assign unit cell parameters to the oriented WAXD pattern. The unit cell that appeared to best fit the data was an orthorhomic unit cell with parameters: 6.40, 4.04 and 32.8 Å for the a, b and c spacings respectively. The calculated reflections are also shown in table 5.3. The theoretical crystalline density for this unit cell is 1.50 g/cc.

4. **Density Measurements**

The density of the orange powder cured at 200°C was estimated to be 1.46±0.01 g/cc while the density of the drawn film was 1.44±0.01 g/cc. The densities of 500 HN Kapton® films before and after thermal treatment were identical according to the floatation technique. To more accurately observe any density differences, both films were placed in the solvent mixture at the same time. No differences in buoyancy could be observed between the two films and the measured density for both films was 1.42±0.01 g/cc.

5. **Thermal Analysis**

The results from DSC measurements on the polyimide powder originating from the straight polyamic solution and 500 HN Kapton® are shown in figure 5.6. The DSC
(Figure 5.4) WAXD pattern for polyimide powder.

(Table 5.2) D-spacings from WAXD pattern for polyimide powder.

<table>
<thead>
<tr>
<th>d-spacings</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$16.48 \pm 0.35 \text{ Å}$</td>
<td>very strong</td>
</tr>
<tr>
<td>$8.14 \pm 0.09$</td>
<td>weak</td>
</tr>
<tr>
<td>$6.41 \pm 0.05$</td>
<td>very strong</td>
</tr>
<tr>
<td>$6.04 \pm 0.05$</td>
<td>very strong</td>
</tr>
<tr>
<td>$5.60 \pm 0.04$</td>
<td>weak</td>
</tr>
<tr>
<td>$4.65 \pm 0.03$</td>
<td>weak</td>
</tr>
<tr>
<td>$4.11 \pm 0.06$</td>
<td>extremely weak</td>
</tr>
<tr>
<td>$3.87 \pm 0.02$</td>
<td>strong</td>
</tr>
<tr>
<td>$3.33 \pm 0.02$</td>
<td>strong</td>
</tr>
<tr>
<td>$3.15 \pm 0.02$</td>
<td>weak</td>
</tr>
<tr>
<td>$3.07 \pm 0.02$</td>
<td>very weak</td>
</tr>
</tbody>
</table>
(Figure 5.5) WAXD pattern for oriented crystalline polyimide film.

(Table 5.3) Measured and calculated d-spacings for oriented crystalline polyimide film. (M = meridional reflection, E = equatorial reflection, blank = off axis reflection)

<table>
<thead>
<tr>
<th>Strength</th>
<th>d-spacings</th>
<th>Location</th>
<th>Calc. d-Spacing</th>
<th>Reflection</th>
</tr>
</thead>
<tbody>
<tr>
<td>very strong</td>
<td>16.36 ± 0.23 Å</td>
<td>M</td>
<td>16.40 Å</td>
<td>0 0 2</td>
</tr>
<tr>
<td>strong</td>
<td>8.12 ± 0.06 Å</td>
<td>M</td>
<td>8.20 Å</td>
<td>0 0 4</td>
</tr>
<tr>
<td>strong (broad)</td>
<td>6.0 - 6.5 Å</td>
<td>(M)</td>
<td>6.40 Å</td>
<td>1 0 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.28 Å</td>
<td>1 0 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.96 Å</td>
<td>1 0 2</td>
</tr>
<tr>
<td>medium</td>
<td>5.52 ± 0.04 Å</td>
<td>M</td>
<td>5.52 Å</td>
<td>1 0 3</td>
</tr>
<tr>
<td>medium</td>
<td>5.51 ± 0.04 Å</td>
<td>M</td>
<td>5.52 Å</td>
<td>1 0 3</td>
</tr>
<tr>
<td>strong</td>
<td>5.47 ± 0.03 Å</td>
<td>M</td>
<td>5.47 Å</td>
<td>0 0 6</td>
</tr>
<tr>
<td>medium</td>
<td>4.09 ± 0.02 Å</td>
<td>M</td>
<td>4.10 Å</td>
<td>0 0 8</td>
</tr>
<tr>
<td>medium</td>
<td>4.03 ± 0.01 Å</td>
<td>E</td>
<td>4.04 Å</td>
<td>0 1 0</td>
</tr>
<tr>
<td>very weak</td>
<td>3.42 ± 0.01 Å</td>
<td>E</td>
<td>3.42 Å</td>
<td>1 1 0</td>
</tr>
<tr>
<td>medium</td>
<td>3.38 ± 0.01 Å</td>
<td>M</td>
<td>3.28 Å</td>
<td>0 0 1 0</td>
</tr>
<tr>
<td>weak</td>
<td>2.96 ± 0.005 Å</td>
<td>M</td>
<td>2.73 Å</td>
<td>0 0 1 2</td>
</tr>
</tbody>
</table>
Figure 5.6) DSC results for polyimide powder cured at 200°C and 500 HN Kapton®.
measurements on the polyimide powder revealed no transitions below 525°C. A broad exotherm began at about 550°C coinciding with the beginning of degradation as shown by the TGA measurement in figure 5.7. A sharp endotherm was clearly visible at 594°C followed by a sharp exothermic upturn in the baseline due to degradation during heating. DSC measurements on 500 HN Kapton® also revealed a sharp but slightly smaller endotherm at 595°C. In the Kapton® sample the exothermic upturn in the baseline occurred at approximately 585°C making quantitative comparison of the two endothermic peaks difficult. Calculations by Bessonov predict the occurrence of a melting point at 597°C for PMDA-ODA polyimides strongly suggesting that the endotherms are due to melting5.

6. Intrinsıc Viscosity Measurements

Figure 5.8 shows a plot of the reduced and inherent viscosities for the polyamic acid in DMAc verses concentration. An intrinsic viscosity of 1.45±0.01 dl/g was measured for the polymer. The weight average molecular weight, $M_w$, was determined to be approximately 74000 g/mol using the Mark-Houwink coefficients determined by Wallach⁶ for PMDA-ODA polyamic acid in DMAc: $[\eta] = 1.85e-4 M_w^{0.8}$.

Figures 5.9 and 5.10 show the intrinsic viscosity measurements for the thermally cured polyimide powder and chemically cured cracked film obtained during run # 5 as listed in table 5.1. The measured zero-time intrinsic viscosities were 0.34 and 0.40 for the powder and film respectively. The weight average molecular weights of the two materials were determined to be 8800 and 12000 g/mol using the Mark-Houwink coefficients found by Wallach³ for PMDA-ODA polyimide in concentrated sulfuric acid: $[\eta] = 2.76e-3 M_w^{0.53}$. 
(Figure 5.7) TGA results for polyimide powder cured at 200°C.
(Figure 5.8) Inherent and reduced viscosity measurements for polyamic acid in DMAc.
(Figure 5.9) Intrinsic viscosity measurements for polyimide powder cured at 200°C and 200 psi.

(Figure 5.10) Intrinsic viscosity measurements for chemically cured polyimide film cured at 200 psi and 200°C.
Although the reasons for the increased crystallinity in polyimides prepared under pressure have not been fully determined, the molecular weight measurements suggest that the increased crystallinity is a result of degradation of the polyamic acid during cure. It is well known that polyamic acids can undergo other side reactions with solvent and water resulting in degradation of the polymer. In many cases where thick polyamic acid films are dried too rapidly, brittle powdery materials are often obtained which have greatly reduced molecular weights. Generally, these side reactions are minimized at lower temperatures but become more important at the higher temperatures. Normally, water and solvent in the system quickly evaporate before significant degradation can occur in the polyamic acid. However, if solvent and water are prevented from leaving the system, such as in the high pressure cure or during rapid curing, degradation of the polyamic acid can occur. The addition of excess anhydride to the polyamic acid solution before thermal treatment did appear to reduce degradation somewhat as evidenced by the viscosity measurements and integrity of the chemically cured films.

The high densities displayed by the pressure cured materials appears to be a result of increased mobility of polyimide chains. This increased mobility is probably, in turn, a result of both the greatly reduced molecular weight due to degradation and the presence of solvent in the system during imidization. Further support of this speculation was found in the insensitivity of the density of Kapton® to the combination of solvent, temperature and pressure. It should be pointed out that the experiments on Kapton® were only performed at 200°C, well below the glass transition temperature of this material. It may be possible for solvent and pressure to have greater effects on crystallinity at temperatures closer to the glass transition temperature.
Experiments and calculations in Chapter II demonstrated that increased chain stiffness increases the ability of polymers to oriented during deformation. The high pressure curing methods discussed in this study may provide means of increasing chain stiffness before solvent removal by increasing the degree of imidization in the gel state. Increased crystallinity can also increase orientation during gel collapse. Although it was possible to obtain swollen films with probably higher imide contents than the chemically cured gels described in Chapter II, so far these films are far too brittle to withstand the drying stresses that develop in the films under biaxial constraint.

There are three possible reasons for the cracking observed in these films. The most probable reason is low molecular weight. Although the molecular weights of films made with 3:1 ratios of curing agents to polyamic acid are unknown, the curing agents had only a minor effect on degradation in films made with 2:1 ratios. Second, the increased crystallinity itself may be the cause of the brittleness. This is not an unusual effect in crystalline polymers. Lastly, the increased imide content of the pressure cured gels probably contributes to the development of significantly higher drying stresses than those encountered in normal chemically cured gel films. During most of the gel collapse in normal gel films, the material is in a rubbery state. Significant drying stress do not develop until concentration of approximately 50% polymer are achieved. The pressure cured gels displayed a leathery texture indicating a higher modulus in the gel state. As a result, stresses probably develop at a much earlier stage in the material even though the total deformation as a result of gel collapse on both materials is identical. Further investigation of these films is required.


CHAPTER VI
SUMMARY AND FUTURE WORK

A. Summary of Conclusions

The main goal of this work has been to identify means of controlling residual stress and dimensional stability in polyimide films. This goal has been the underlying theme for the first three data chapters. The last data chapter, concerning the characterization of crystalline polyimides, was largely an outgrowth of results found in Chapter II. Although the majority of the work presented in this dissertation has been performed on polyimides, many of the analyses and conclusions were based on continuum arguments and, as a result, can apply to a broad class of materials. This is especially true of work presented in Chapters III and IV. A few of the main results and conclusions of this overall study on polyimides are summarized below.

In Chapter II, the effects of different curing techniques on the cooling stresses were investigated and the relationship between the curing temperature and final residual stress in uniaxial and biaxial constrained coatings was demonstrated. It was found that residual stresses could be modified through the thermal expansion coefficient of the polyimide coating by controlling molecular orientation with respect to the coating surface. Polyimide films made by the chemically cured gel technique demonstrated lower in-plane thermal expansion coefficients and greater out-of-plane birefringences than films made by thermal curing as a result of greater orientation with respect to the film surface. Calculations based on Roe and Krigbaum's segmental orientation model suggest that the increased orientation was due to greater chain stiffness from partial imidization prior to gel collapse.
The investigation of stresses in polyimide films was extended to consider stresses arising during the processing of films on tenter frames. The state of stress in films processed on tenter frames was found to be very similar to the stress state found in coatings under biaxial constraints with the exception of an in-plane shear stress that varied linearly across the width of the line. It was found that this shear stress was a result of gradients in the normal stresses occurring along the machine direction and was responsible for the parabolic displacement profiles and non-uniform and anisotropic orientation behavior typically found in films made on tenter frames. The maximum shear stresses are always found at the edges of a tenter frame and as a result, wider tenter frames are subject to greater problems with stress anisotropy and non-uniformity. The stress gradients were found to arise from gradients in processing conditions such as temperature or solvent concentration, but could be eliminated or at least reduced by the application of different types of external strain.

The effects of cooling stresses on dimensional stability were investigated in Chapter III. Irreversible shrinkage in polyimide films was found to be a direct result of the stress history developed during cooling. Although cooling stress behavior in PMDA-ODA films are usually found to be rate independent, linear thermo-viscoelasticity quantitatively described strain storage and shrinkage behavior in both thermally cured PMDA-ODA and Upilex® polyimide films.

One of the interesting findings during the study of gelation in polyimides was a highly crystalline powder form of PMDA-ODA. Although molecular weight measurements indicate that the powder is probably formed as a result of major degradation of the polyamic acid precursor during cure, the high degree of order and isotropic nature of the powder make it potentially useful for the characterization of crystallinity and structure properties relationships in polyimide materials. Although most attempts to make highly crystalline films were unsuccessful due to degradation, it was possible to make partially crystalline films that were drawable at high temperatures.
B. Future Work

The work presented in this thesis has intentionally covered a wide variety of topics relating to polyimide processing. Although many of the studies could certainly stand further examination, two topics in particular should require further investigation.

The first topic is the study of irreversible shrinkage and its relationship to stress and thermal history. Although irreversible shrinkage is an important aspect of polymeric behavior that is encountered in many different polymer technologies, very few comprehensive techniques exist for the prediction of this behavior. The relationships between shrinkage and stress discussed in this work have so far only been applied to mechanically simple and well-behaved materials under very limited circumstances. These studies of shrinkage could easily expand to investigate effects of crystallization, aging and other effects that cause the behavior of the material to change during use. These types of effects could conceivably be accounted for by adding extra thermodynamic parameters to the viscoelastic equations so far discussed.

Another aspect of stored strain behavior that should be discussed is the effects of stored strain on stress. The behavior of materials under zero non-constrained conditions was used as a basis for quantifying results and making predictions. However, in practice, polyimide films are subjected to two and sometimes even three-dimensional constraints while shrinkage occurs. Although it was shown that shrinkage behavior results in extra stress development during the cooling of these materials, a direct effect of stored strain release on stress development has yet to be demonstrated. Experiments and modeling along these lines could easily be performed using the tools developed in this study.

The second area of this work that requires further investigation is the characterization and development of the crystalline polyimide powders and films
discussed in Chapter V. The work presented in Chapter V was only meant as a preliminary characterization of the crystalline materials and many questions about the morphology and origin of the materials still exist. These studies should include a more detailed x-ray characterization and infrared spectroscopy of the materials as well. More work should also be done to investigate the effects of pressure and solvents on fully cured polyimides as well.

Although attempts to make crystalline polyimide films were not entirely successful using high pressure techniques, it may still be possible to do so. So far it is unclear as to why the resulting films are so brittle. Three possible reasons that were discussed earlier are degradation, large drying stresses or decreased strength from crystallinity. An investigation into these potential causes could be interesting. If highly crystalline can be made, they could also be useful for the investigation of crystallinity on orientation behavior in polyimides.

Although the effects of many different processing variables on tenter frame stress profiles were discussed at length in Chapter IV, a few important factors were left out of this analysis such as changes in material properties during processing and the effects of orientation profiles on stress development. Unfortunately, analytic treatment of these factors is extremely difficult and quantitative analysis would require methods such a finite element analysis. Although a more quantitative stress analysis of tenter frames may be useful, a more direct and probably more beneficial approach would be to develop techniques for on line measure stresses and orientation. Such measurements could be used in conjunction with the concepts developed here to establish better control of material properties and shrinkage.
APPENDIX A

ACCOUNTING FOR INTERNAL REFLECTION IN BIREFRINGENCE MEASUREMENTS

In Chapter II a technique was described to measure the out-of-plane birefringence of a coating on a reflective substrate. This technique consisted of reflecting a plane-polarized laser beam off the substrate and measuring the resulting retardation of the beam with a Babinet compensator (Figure 2.4). One of the main assumptions made when making these birefringence measurements was that the reflected beam was composed only or at least mostly light reflecting only once off the substrate surface. In reality, the reflected light is a composite of many orders of reflections from both the substrate and film surface as shown in figure A.1. The purpose of this analysis is to evaluate the effects of internal reflection on the final measured retardation and to determine conditions in which such effects may be minimized.

The analysis will be performed using the Fresnel equations describing the reflection and transmission of light off and through optically thick coatings. For further discussion of mathematical treatment of this phenomena, a good source is Azzam and Bashara's *Ellipsometry and Polarized Light*. It will be assumed that absorption of light by the coating is minimal. The reddish color of PMDA-ODA polyimides indicates that the coating is largely transparent to red light. Since the wavelength of light used in these measurements is 6328Å, minimal absorption appears to be a valid assumption.

The electric field vector of the incident plane-polarized monochromatic light beam can be represented in terms of two orthogonal components as follows:
(Figure A.1) Schematic of internal reflection resulting from an optically thick coating on a reflective substrate.
\[ \mathbf{E}_0 = \hat{i}E_{x_0}e^{i(kz-\omega t)} + \hat{j}E_{y_0}e^{i(kz-\omega t)} \]  

(A.1)

where light waves are traveling along the z-direction, the x-direction is parallel to the coating surface and the y-direction is orthogonal to both the x and z-directions. The terms, \( k \) and \( \omega \) are the wave number and frequency of the light wave and \( E_{x_0} \) and \( E_{y_0} \) are the amplitudes of the electric field components in the x and y directions. The field intensities in the x and y directions are simply the squares of the amplitudes and the total intensity of a given light wave is simply: \( I = (E_x^2 + E_y^2) \). Since the incident beam is plane polarized at a direction 45° to the x-direction, \( E_x = E_y = E_0 \) and the two electric field components are in phase with one another.

When the incident beam meets the coating surface, part of the beam is reflected from the coating-air interface with resulting field amplitudes \( E_{x_1} \) and \( E_{y_1} \) and the rest is transmitted through the coating with amplitudes \( E'_{x_1} \) and \( E'_{y_1} \) as shown in figure A.1. Since the substrate is assumed to be a perfect reflector, the entire transmitted beam is reflected back to the coating-air interface where again part is transmitted with field amplitudes \( E_{x_2} \) and \( E_{y_2} \) and the rest is reflected back into the coating. This operation can continue indefinitely.

Whenever the beam passes through the coating, the two components of the electric field vector experience phase shifts given by \( \delta_x \) and \( \delta_y \) due to differences in the optical path length of the two components. The retardation of the beam is defined as \( \Delta = \delta_x - \delta_y \). The expression for light reflected from the substrate only once and transmitted through the coating-air interface is:

\[ \mathbf{E}_2 = \hat{i}E_{x_1}e^{i(kz-\omega t+\delta_x)} + \hat{j}E_{y_2}e^{i(kz-\omega t+\delta_y)} \]  

(A.2)

Light reflected from the substrate is a composite of reflected light waves with varying field magnitudes and phase shifts. The components of the composite field
vector are simply the sum of the individual reflected field vectors. As a result, the overall phase shifts of the composite beam, $\delta_x$ and $\delta_y$, can be found by:

$$\begin{align*}
\left( \sum_{j=1}^{\infty} E_{x_j} \right) e^{i\delta_x} &= E_{x_1} + E_{x_2} e^{i\delta_x} + E_{x_3} e^{i2\delta_x} + \ldots \\
\left( \sum_{j=1}^{\infty} E_{y_j} \right) e^{i\delta_y} &= E_{y_1} + E_{y_2} e^{i\delta_y} + E_{y_3} e^{i2\delta_y} + \ldots
\end{align*}$$

(A.3)

where $E_{x_j}$ and $E_{y_j}$ are the amplitudes for the various beams reflected from the coating.

Equation A.3 can be expressed in trigonometric form as well:

$$\begin{align*}
\left( \sum_{j=1}^{\infty} E_{x_j} \right) \cos \delta_x + i \sin \delta_x &= \left( \sum_{j=1}^{\infty} E_{x_j} \right) \left[ \cos((j-1)\delta_x) + i \sin((j-1)\delta_x) \right] \\
\left( \sum_{j=1}^{\infty} E_{y_j} \right) \cos \delta_y + i \sin \delta_y &= \left( \sum_{j=1}^{\infty} E_{y_j} \right) \left[ \cos((j-1)\delta_y) + i \sin((j-1)\delta_y) \right].
\end{align*}$$

(A.4)

If equation A.4 is separated into real and imaginary components, the composite phase shifts can be found in terms of the phase shifts, $\delta_x$ and $\delta_y$, and the electric fields, $E_{x_j}$ and $E_{y_j}$ of the individual reflections:

$$\tan \delta_x = \frac{\sum_{j=1}^{\infty} E_{x_j} \sin((j-1)\delta_x)}{\sum_{j=1}^{\infty} E_{x_j} \cos((j-1)\delta_x)} \quad \tan \delta_y = \frac{\sum_{j=1}^{\infty} E_{y_j} \sin((j-1)\delta_y)}{\sum_{j=1}^{\infty} E_{y_j} \cos((j-1)\delta_y)}.$$

(A.5)

The phase shifts for each reflection can be determined by finding the difference in path lengths between two adjacent reflections and multiplying the difference by $4\pi n_i/\lambda$ where $\lambda$ is the wavelength of light and $n_i$ is refractive index of the coating at directions orthogonal to the direction of light travel (x or y). The path length difference between reflections is $2d/cos\theta'$ and the resulting phase shifts are:
\[ \delta_x = \frac{4\pi dn_x}{\lambda \cos \theta'} \quad \text{and} \quad \delta_y = \frac{4\pi dn_y}{\lambda \cos \theta'} \] (A.6)

where \( d \) is the coating thickness and \( \theta' \) is the angle between the direction of travel of the refracted light wave and the normal to the coating surface. The refracted angle, \( \theta' \), is related to the incident angle, \( \theta \), through Snell's Law: \( n \sin \theta' = \sin \theta \) where \( n \) is the mean refractive index of the coating. The refractive indices \( n_x \) and \( n_y \) can be related to the refractive indices parallel and perpendicular to the coating surface by a simple tensor rotation to a 1,2,3-coordinate system, also defined in figure A.1 where the 1 and 2-directions are parallel to the coating surface and the 3-direction is perpendicular to the surface. The resulting phase shifts are:

\[ \delta_x = \frac{4\pi dn_1}{\lambda \cos \theta'} \quad \text{and} \quad \delta_y = \frac{4\pi d}{\lambda \cos \theta'} (n_1 \cos^2 \theta' + n_3 \sin^2 \theta') \] (A.7)

where the coating is assumed to be planar isotropic and uniform through the thickness.

The field amplitudes, \( E_{x_1} \) and \( E_{x_1} \), can be found using Fresnel's equations for reflection and transmission. These equations are listed below:

\[
\begin{align*}
\frac{E_{x_1}}{E_{x_0}} &= r_x = \frac{n \cos \theta - \cos \theta'}{n \cos \theta + \cos \theta'} \\
\frac{E_{y_1}}{E_{y_0}} &= r_y = \frac{\cos \theta - n \cos \theta'}{\cos \theta + n \cos \theta'} \\
\frac{E'_{x_1}}{E'_{x_0}} &= t_x = \frac{2 \cos \theta}{n \cos \theta + \cos \theta'} \\
\frac{E'_{y_1}}{E'_{y_0}} &= t_y = \frac{2 \cos \theta}{\cos \theta + n \cos \theta'} \\
\frac{E_{x_1}}{E'_{x_{1+}}'} &= r'_{x} = \frac{n \cos \theta' - \cos \theta}{n \cos \theta' + \cos \theta} \\
\frac{E_{y_1}}{E'_{y_{1+}}'} &= r'_{y} = \frac{\cos \theta' - n \cos \theta}{\cos \theta' + n \cos \theta} \\
\frac{E'_{x_1}}{E'_{x_{1+}}'} &= t'_{x} = \frac{2 \cos \theta'}{n \cos \theta' + \cos \theta} \\
\frac{E'_{y_1}}{E'_{y_{1+}}'} &= t'_{y} = \frac{2 \cos \theta'}{\cos \theta' + n \cos \theta} 
\end{align*}
\] (A.8)
The terms \( r_i \) and \( t_i \) represent reflections and transmissions from the air side of the coating-air interface and \( r'_i \) and \( t'_i \) represent reflections and transmissions from the coating side of the interface where \( i = x \) or \( y \). The amplitudes can then be expressed in terms of the incident amplitude, \( E_0 \), and the various reflection and transmission operations:

\[
\begin{align*}
E_{x_i} &= r_x E_0 \\
E_{x_j} &= t_x t'_x r_x^{(j-2)} E_0 \\
E_{y_i} &= t_y E_0 \\
E_{y_j} &= t_y t'_y r_y^{(j-2)} E_0.
\end{align*}
\]

The resulting phase shifts are:

\[
\tan \delta_x = \frac{t_x t'_x \sum_{j=1}^{\infty} r_x^{(j-1)} \sin(j \delta_x)}{r_x + t_x t'_x \sum_{j=1}^{\infty} r_x^{(j-1)} \cos(j \delta_x)} \quad \tan \delta_y = \frac{t_y t'_y \sum_{j=1}^{\infty} r_y^{(j-1)} \sin(j \delta_y)}{r_y + t_y t'_y \sum_{j=1}^{\infty} r_y^{(j-1)} \cos(j \delta_y)}.
\]

The reflected intensities resulting from a light wave 45° incident to the surface normal reflecting off a coating with a mean refractive index of 1.75 are shown in figure A.2. The Fresnel equations estimate that approximately 58% of the measured beam intensity comes from light reflected once off the substrate. The balance of the signal comes from light reflected from the coating-air interface and internal reflections. Similar results were observed for lights waves 30 to 60° incident to the coating surface.

The errors in retardation measurements due to the disregard of internal reflections were calculated for 4 different incident angles between 30 and 60° and are shown in figures A.3 through A.6. For each incident angle, errors were calculated for thicknesses ranging between 1 and 200 \( \mu m \) and birefringences between 0 and -0.20 with a mean refractive index for PMDA-ODA of 1.75. The calculations showed errors greater...
(Figure A.2) Calculated relative intensities for multiple reflections of light from polyimide coating.
(Figure A.3) Errors under various thickness and birefringence conditions as a result of assuming no internal reflection in birefringence measurements with 30° incident light source.

(Figure A.4) Errors under various thickness and birefringence conditions as a result of assuming no internal reflection in birefringence measurements with 37° incident light source.
(Figure A.5) Errors under various thickness and birefringence conditions as a result of assuming no internal reflection in birefringence measurements with 45° incident light source.

(Figure A.6) Errors under various thickness and birefringence conditions as a result of assuming no internal reflection in birefringence measurements with 60° incident light source.
than 20% occurring at large thicknesses and at small birefringences but decreased with increasing angle with respect to the surface normal.
APPENDIX B

SOURCE CODE LISTING FOR TMAANAL3.BAS

This program was written to allow easy manipulation of data obtained from the TA Instruments 2940 thermal mechanical analyzer (TMA). Data from the TMA is saved in a binary format and can be transferred to a DOS using the "User Programmability Software" included with the TMA setup or using a standard disk editor. The program listed here accesses data in the binary format, converts the data to a decimal format and allows calculation of thermal expansion and stress-temperature coefficients as a function of temperature. The slopes within prespecified regions are calculated using a linear regression routine. Data is saved in a parsed ASCII format compatible with various spreadsheet software programs.

'**********************************************************************************************
'PROGRAM: TMAANAL3.BAS
'FINAL VERSION: 6/19/92
'WRITTEN BY: ROBERT JENNINGS
'
'DESCRIPTION: THIS PROGRAM ANALyzES DATA COLLECTED ON THE TA INSTRUMENTS 2940 TMA. BINARY FILES CREATED BY THE TMA AND SAVED IN DOS CAN BE READ DIRECTLY AND SLOPES VERSES TEMPERATURE CAN BE CALCULATED. OUTPUT DATA IS SAVED IN A PARSED, ASCII FORMAT READABLE BY EXCEL AND OTHER SPREADSHEETS.
'**********************************************************************************************

DIM AS(21), D(4000, 3), TC(4000), SC(4000)

'******PARAMETER DEFINITIONS**************************

'STRING VARIABLES:
' A$,BS$ = GENERAL KEYBOARD INPUT
' CS$,DS,F1$ = FILE BINARY INPUT
' FS$,FO$ = INPUT AND OUTPUT FILENAMES
' FF2ES$,FF2SS$,FF3$,FF4$,FF5$,FF6$ = OPERATION FLAGS

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THS, WIS = THICKNESS AND WIDTH INPUTS
XTIT$ = X-AXIS TITLE
YTIT1$ = Y-AXIS TITLE #1
YTIT2$ = Y-AXIS TITLE #2
XUN$, YUN$ = UNITS OF X AND Y-AXES

'INTBERS
I%, II%, J%, K% = GENERAL COUNTING
NCHAN% = NUMBER OF DATA CHANNELS
N% = NUMBER DATA POINTS
ED% = NUMBER OF DATA LINES
R% = COUNTING DURING SLOPE CALCULATIONS
UR%, LR% = UPPER AND LOWER RANGES FOR LOCALIZED SLOPE CALCULATIONS

'CONSTANTS
A = GENERAL KEYBOARD INPUT
DP = LENGTH OF FILE
DT = MINIMUM TEMPERATURE INCREMENT
L = SAMPLE LENGTH
PP = TITLE POSITIONING CONSTANT
TH = SAMPLE THICKNESS
WI = SAMPLE WIDTH
SLT = DEFINITION OF SLOPE CALCULATION (STRAIN OR STRESS)
SCMIN, SCMAX = MINIMUM AND MAXIMUM STRESS-TEMPERATURE COEFFICIENTS
STEM = SUM OVER LOCAL TEMPERATURE DATA
STEM2 = SUM OVER LOCAL TEMPERATURE DATA SQUARED
SSTR = SUM OVER LOCAL STRESS OR STRAIN DATA
STS = SUM OVER LOCAL TEMPERATURE STRESS/STRAIN PRODUCTS
TMIN, TMAX = MINIMUM AND MAXIMUM TEMPERATURES
TCMIN, TCMAX = MINIMUM AND MAXIMUM THERMAL EXPANSION COEFFICIENTS
X PLOT, Y PLOT = PLOTTING VALUES

X, Y = PLOTTING COORDINATES (SCREEN SPACE)
XX, YY = DEFINITIONS OF PLOT DATA
XMIN, XMAX = RANGE SETTINGS FOR X-AXIS
YMIN, YMAX = RANGE SETTINGS FOR Y-AXIS
LFT, RGT = LEFT AND RIGHT PLOT BORDERS
BTM, TOP = UPPER AND LOWER PLOT BORDERS

'ARRAYS:
A$(M) = FILE HEADER INFORMATION
D(N, NCHAN%) = RAW DATA
SC(N) = CALCULATED STRESS/TEMPERATURE COEFFICIENTS
TC(N) = CALCULATED THERMAL EXPANSION COEFFICIENTS

'************ MAIN MENU ************
COLOR 1: PRINT TAB(15 + PP); "É"; : FOR I = 1 TO 44: PRINT "Í"; : NEXT I: PRINT "";
PRINT TAB(15 + PP); ""; : COLOR 4: PRINT TAB(27 + PP); "TMA Data Analyzer 3.0";
COLOR 1: PRINT TAB(60 + PP); "";
PRINT TAB(15 + PP); ""; : PRINT TAB(60 + PP); "";
PRINT TAB(15 + PP); ""; : COLOR 4
PRINT TAB(19 + PP); "Written by Robert Jennings on 12/21/91"; : COLOR 1
PRINT TAB(60 + PP); "";
PRINT TAB(15 + PP); "";
PRINT TAB(19 + PP);
"«";
COLOR 1
PRINT TAB(60 + PP);
"";
PRINT TAB(15 + PP);
PRim
PRINT TAB(60 + PP);
"";
PRINT TAB(15 + PP);
"";
PRINT TAB(19 + PP);
"Written by Robert Jennings on 12/21/91";
PRINT "";
COLOR 2
PRINT TAB(10); "Options:"; PRINT
PRINT TAB(15); "<D> Directory"
IF FF1$ = "DONE" THEN COLOR 5
PRINT TAB(15); "<L> Load File": COLOR 2
IF FF2ES = "DONE" OR FF2SS = "DONE" THEN COLOR 5
IF FF2ES = "CANT" OR FF2SS = "CANT" THEN COLOR 7
PRINT TAB(15); "<T> Calculate Slopes vs Temperature": COLOR 2
IF FF3$ = "DONE" THEN COLOR 5
IF FF3$ = "CANT" THEN COLOR 7
PRINT TAB(15); "<C> Change Sample Dimensions": COLOR 2
IF FF5$ = "CANT" THEN COLOR 7
PRINT TAB(15); "<P> Plot Data": COLOR 2
IF FF6$ = "DONE" THEN COLOR 5
IF FF6$ = "CANT" THEN COLOR 7
PRINT TAB(15); "<S> Save Data": COLOR 2
PRINT TAB(15); "<Q> Quit"
PRINT

'**********MAIN MENU INPUT******************************************************************************************

50 AS = INKEYS: IF AS = "" THEN 50
IF AS = "d" OR AS = "D" THEN GOTO 70
IF AS = "L" OR AS = "l" THEN GOTO 100
IF AS = "t" OR AS = "T" THEN GOSUB 1000: GOTO 1
IF AS = "c" OR AS = "C" THEN GOSUB 7000: GOTO 1
IF AS = "p" OR AS = "P" THEN GOSUB 3000: GOTO 1
IF AS = "s" OR AS = "S" THEN GOSUB 400: GOTO 1
IF AS = "q" OR AS = "Q" THEN 60
GOTO 50

60 PRINT "Are you sure (Y/N)?"
65 AS = INKEYS: IF AS = "" THEN 65
IF AS = "n" OR AS = "N" OR ASC(AS) = 27 THEN 1
IF AS <> "Y" AND AS <> "y" THEN 65
PRINT TAB(25); "Have a nice day! "; Chr$(1): END

70 '**********DRIVE DIRECTORY******************************************************************************************

PRINT "Which drive? "; : GOSUB 20000: IF ASC(AS) = 27 THEN 1
AS = BS
IF RIGHT$(A$, 1) <> "\" THEN A$ = A$ + "\n"
ON ERROR GOTO 80
CLS : PRINT : PRINT "Directory of "; A$
PRINT : FILES A$ + ":*:"
ON ERROR GOTO 0
PRINT : PRINT TAB(27); "Hit any key to continue." 
75 A$ = INKEY$: IF A$ = "" THEN 75
GOTO 1

****DISK ERROR MESSAGES************************
80 PRINT : IF ERR <> 57 THEN 81
   PRINT "I/O error - Possible disk problem."
   RESUME 75
81 IF ERR <> 71 THEN 82
   PRINT "Disk not ready - Check the disk and try again."
   RESUME 75
82 IF ERR <> 76 THEN 83
   PRINT "Path not found - Try again."
   RESUME 75
83 IF ERR <> 72 THEN 84
   PRINT "Your disk has at least one bad sector - Try another disk."
   RESUME 75
84 IF ERR <> 75 THEN 90
   PRINT "Path Access Error - Try again."
   RESUME 75
90 CLS : PRINT : PRINT : PRINT "There is an error...": PRINT " ERR ="; ERR; " ERL ="; ERL
91 A$ = INKEY$: IF A$ = "" THEN 91
   PRINT : PRINT "Don't look at me, I don't know what the problem is."
   PRINT "You made the mistake!"
92 A$ = INKEY$: IF A$ = "" THEN 92
END

100 "********Loading File**************************
   IF FF1$ <> "DONE" THEN 110
   PRINT "Clear current file (Y/N)?"
105 A$ = INKEY$: IF A$ = "" THEN 105
   IF A$ = "N" OR A$ = "n" OR ASC(A$) = 27 THEN 1
   IF A$ = "Y" OR A$ = "y" THEN CLOSE : GOTO 110
   GOTO 105
110 PRINT "Source Filename: "; : GOSUB 20000: IF ASC(A$) = 27 THEN GOTO 1
   FS = B$
111 ON ERROR GOTO 370
   OPEN "I", #1, FS
   ON GOTO ERROR 0
   PRINT : PRINT "Minimum temperature increment (°C): "; : GOSUB 20000
   IF ASC(A$) = 27 THEN CLOSE : GOTO 110
   DT = VAL(B$)
   PRINT
   "****HEADER INFORMATION**********
   FOR I% = 1 TO 16
      INPUT #1, A$(I%): PRINT A$(I%)
   NEXT I%
   PRINT : PRINT
   WS = "": THS = ""
   FOR J% = 1 TO LEN(A$(3)) - 1
C$ = MIDS(A$(3), J%, 2)
IF C$ <> "W=" AND C$ <> "w=" THEN 120
K% = J% + 2

115  C$ = MIDS(A$(3), K%, 1)
IF (ASC(C$) < 48 OR ASC(C$) > 57) AND ASC(C$) <> 46 THEN 120
    WIS = WIS + C$
    K% = K% + 1
    IF K% > LEN(A$(3)) - 1 THEN J% = LEN(A$(3)): GOTO 130
    GOTO 115

120  IF C$ <> "T=" AND C$ <> "t=" THEN 130
K% = J% + 2

125  C$ = MIDS(A$(3), K%, 1)
IF (ASC(C$) < 48 OR ASC(C$) > 57) AND ASC(C$) <> 46 THEN 130
    TH$ = TH$ + C$
    K% = K% + 1
    IF K% > LEN(A$(3)) - 1 THEN J% = LEN(A$(3)): GOTO 130
    GOTO 125

130 NEXT J%
    L = VAL(MIDS(A$(4), 6, 6)): PRINT "Initial Sample Length (mm):": ; PRINT USING "###.###": L
131  WI = VAL(WIS): PRINT "Sample Width (mm):": ; PRINT USING "###.###": WI
    TH = VAL(THS): PRINT "Sample Thickness (µm):": ; PRINT USING "###.###": TH

135 IF WI <> 0 THEN 136
    PRINT
    PRINT "Sample Width (mm): ";
    GOSUB 20000
    IF ASC(A$) = 27 THEN CLOSE : PRINT : GOTO 110
    WI = VAL(B$): PRINT

136 IF TH <> 0 THEN 139
    PRINT "Sample Thickness (µm): ";
    GOSUB 20000
    IF ASC(A$) = 27 THEN PRINT : GOTO 135
    TH = VAL(B$)

139 PRINT : PRINT TAB(28); "Hit any key to continue."
140 A$ = INKEY$: IF A$ = "" THEN 140

*****RAW DATA INPUT AND CONVERSION TO DECIMAL NUMBERS************
NCHAN% = 4
OPEN "R", #3, FS$, 1
FIELD #3, 1 AS F1$S
I% = 1
WHILE ASC(F1$S) <> 12
    GET #3, I%
    I% = I% + 1
WEND
DP = LOC(3) + 2
ED% = INT((LOF(3) - DP) / NCHAN% / 4)
B$ = ": DS = "
LSET F1$S = " "
I% = 1: II% = 1
WHILE NOT EOF(3)
145  FOR J% = 1 TO NCHAN%
    FOR K% = 1 TO 4
        GET #3, DP
        BS = BS + F1$S
    NEXT K%
NEXT J%
$$DP = DP + 1$$

$$\text{NEXT } K\%$$

$$D\% = B\%$$

$$J\% = 1$$

$$\text{DA}(J\%) = \text{CVS}(\text{MID$$(D\%,J\%*4 - 3,4))$$}$$

$$\text{IF } \text{ABS} (\text{DA}(J\%)) > 10000! \text{ THEN } 275$$

$$J\% = J\% + 1$$

$$\text{IF } J\% < 5 \text{ THEN } 147$$

$$\text{IF } \text{ABS} (\text{DA}(2) - D(II\% - 1, 1)) < DT \text{ AND } II\% > 1 \text{ THEN } 260$$

$$D(II\%, 0) = \text{DA}(1)$$

$$D(II\%, 1) = \text{DA}(2)$$

$$D(II\%, 2) = \text{DA}(3) / L / 10$$

$$D(II\%, 3) = \text{DA}(4) / WI / TH * 1000$$

$$\text{IF } II\% = 1 \text{ THEN } \text{GOSUB } 350$$

$$\text{XPL0T} = D(II\%, 1)$$

$$\text{YPL0T} = D(II\%, 2)$$

$$\text{GOSUB } 10500$$

$$II\% = II\% + 1$$

$$I\% = I\% + 1$$

$$\text{IF } II\% > 4000 \text{ THEN PRINT : PRINT TAB(10); "I ran out of memory." : GOTO 275}$$

$$B\% = ""$$

$$270 \text{ WEND}$$

$$275 \text{ N\%} = II\% - 1$$

$$300 \text{ FF1\$} = "\text{DONE}"$$

$$\text{FF2E\$} = "": \text{FF2S\$} = "": \text{FF3S\$} = "": \text{FF4\$} = "": \text{FF5\$} = "": \text{FF6\$} = ""$$

$$\text{LOCATE } 3, 29: \text{PRINT } \text{"Hit any key to continue."}$$

$$310 \text{ A\$} = \text{INKEYS}: \text{IF } A\% = "" \text{ THEN } 310$$

$$320 \text{ CLOSE } #1: \text{SCREEN } 0: \text{COLOR } 10: \text{GOTO } 1$$

$$350 \text{ XMIN} = 0: \text{XMAX} = 400$$

$$\text{YMIN} = -2$$

$$\text{YMAX} = 2$$

$$\text{XTIT}\$ = \text{"Temperature } (^\circ \text{C})": \text{ytit2}\$ = \text{" Strain"}: \text{YTIT1}\$ = "": \text{YUN}\$ = "(\%)"$$

$$\text{GOSUB } 10000$$

$$\text{LOCATE } 1, 25: \text{PRINT } \text{"Just a minute. Formatting Data..."}$$

$$\text{LOCATE } 2, 23: \text{PRINT } \text{"This should take about"};$$

$$\text{PRINT USING } \text{"##.##"; LOF(1) * 2.3 / 17500;}: \text{PRINT } \text{" minutes." \ RETURN}$$

"*****DISK ERROR MESSAGES********************

370 \text{PRINT : IF } \text{ERR} <> 57 \text{ THEN } 372$$

$$\text{PRINT } \text{"I/O error  - Possible disk problem or share violation."}$$

$$\text{RESUME } 310$$

372 \text{IF } \text{ERR} <> 55 \text{ THEN } 374

$$\text{PRINT } \text{"File already exists  - Try another name."}$$

$$\text{RESUME } 310$$

374 \text{IF } \text{ERR} <> 61 \text{ THEN } 376

$$\text{PRINT } \text{"Disk full  - Try another disk."}$$

$$\text{RESUME } 310$$

376 \text{IF } \text{ERR} <> 67 \text{ THEN } 378

$$\text{PRINT } \text{"Too many files in disk directory  - Try another disk."}$$

$$\text{RESUME } 310$$

378 \text{IF } \text{ERR} <> 70 \text{ THEN } 380
PRINT "This disk is write protected - Try another disk."
RESUME 310
380 IF ERR <> 71 THEN 382
    PRINT "Disk not ready - Check the disk and try again."
    RESUME 310
382 IF ERR <> 76 THEN 384
    PRINT "Path not found - Try again."
    RESUME 310
384 IF ERR <> 53 THEN 385
    PRINT "I couldn't find your file - Check the name and try again."
    RESUME 310
38 IF ERR <> 72 THEN 386
    PRINT "Your disk has at least one bad sector - Try another disk."
    RESUME 310
386 IF ERR <> 75 THEN 387
    PRINT "Path Access Error - Try again."
    RESUME 310
387 cls : PRINT : PRINT : PRINT "There is an error...": PRINT " ERR ="; ERR; " ERL ="; ERL:
        PRINT : PRINT "Don't look at me, I don't know what the problem is."
        PRINT "You made the mistake!"
388 AS = INKEYS: IF AS = "" THEN 388
END

400 '**********Saving Data*****************************************************
    IF FF6$ = "CANT" THEN PRINT "No data to save": GOTO 950
    PRINT : PRINT "Output Filename: "; : GOSUB 20000: IF ASC(A$) = 27 THEN 1
        fo$ = B$
405 ON ERROR GOTO 970
    OPEN "O", #2, fo$
    ON ERROR GOTO 1
    PRINT : PRINT " Saving Data..."
    FOR 1% = 1 TO 6
        PRINT #2, A$(1%)
        NEXT 1%
        PRINT #2, 
            " Length="; CHR$(9); L; CHR$(9); "mm"
        PRINT #2, 
            " Width="; CHR$(9); W1; CHR$(9); "mm"
        PRINT #2, 
            "Thickness ="; CHR$(9); TH; CHR$(9); "m"
    FOR 1% = 13 TO 16
        PRINT #2, A$(1%)
        NEXT 1%
        PRINT #2,
            PRINT #2, "Time": CHR$(9); "Temp": CHR$(9); "Strain": CHR$(9); "Stress";
            IF FF2E$ = "DONE" THEN PRINT #2, CHR$(9); "TEC";
            IF FF2S$ = "DONE" THEN PRINT #2, CHR$(9); "ds/dT";
            PRINT #2,
            PRINT #2, 
                "-------------------"; CHR$(9); 
                "-------------------"; CHR$(9); "-------------------";
                IF FF2E$ = "DONE" THEN PRINT #2, CHR$(9); "-------------------";
                IF FF2S$ = "DONE" THEN PRINT #2, CHR$(9); "-------------------";
                PRINT #2,
                FOR 1% = 1 TO N%
                    PRINT #2, D(I%, J% - 1); CHR$(9);
                    NEXT J%
                    IF FF2E$ = "DONE" THEN PRINT #2, TC(I%); CHR$(9);
IF FF2$ = "DONE" THEN PRINT #2, SC(I%); PRINT #2,
NEXT I%
FF6$ = "DONE"
900 CLOSE #1: CLOSE #2
FF9$ = "DONE": RETURN
950 A$ = INKEY$: IF A$ = "" THEN 950 RETURN

'****DISK ERROR MESSAGES**********************
970 IF ERR <> 57 THEN 972
PRINT "I/O error - Possible disk problem or share violation."
RESUME 950
972 IF ERR <> 55 THEN 974
PRINT "File already exists - Try another name."
RESUME 950
974 IF ERR <> 61 THEN 976
PRINT "Disk full - Try another disk."
RESUME 950
976 IF ERR <> 67 THEN 978
PRINT "Too many files in disk directory - Try another disk."
RESUME 950
978 IF ERR <> 70 THEN 980
PRINT "This disk is write protected - Try another disk."
RESUME 950
980 IF ERR <> 71 THEN 982
PRINT "Disk not ready - Check the disk and try again."
RESUME 950
982 IF ERR <> 76 THEN 984
PRINT "Path not found - Try again."
RESUME 950
984 PRINT "There is an error...ERR ="; ERR; " ERL ="; ERL
PRINT "Don't look at me, I don't know what the problem is."
PRINT "You made the mistake!"
986 A$ = INKEY$: IF A$ = "" THEN 986 END

1000 '********Calculating Slopes vs Temperature**************
IF FF1$ <> "DONE" THEN PRINT "No data for slope calculation."
: GOTO 1950
PRINT : PRINT "Strain <e> or Stress <s> vs temperature?"
1010 A$ = INKEY$: IF A$ = "" THEN 1010
IF A$ = "E" OR A$ = "e" THEN SLT = 2: GOTO 1020
IF A$ = "S" OR A$ = "s" THEN SLT = 3: GOTO 1020
IF ASC(A$) = 27 THEN 1950
1020 PRINT "Temperature range for each slope calculation (nR90C): "; GOSUB 20000
IF ASC(A$) = 27 THEN RETURN
RT = VAL(B$)
R% = 0
1040 R% = R% + 1
IF ABS(D(R% + 1, 1) - D(0, 1)) < RT THEN 1040
STEMP = 0: STS = 0: SSTR = 0: STEM2 = 0:
TMIN = 1E+38: TMAX = -1E+38: TCMIN = 1E+38: TCMAK = -1E+38: SCMIN = 1E+38
SCMAX = -1E+38
FOR J% = 0 TO R% - 1
\[
STEMP = STEM + D(J\%, 1)
\]
\[
STEM2 = STEM2 + D(J\%, 1) \cdot 2
\]
\[
SSTR = SSTR + D(J\%, SLT)
\]
\[
STS = STS + D(J\%, 1) \cdot D(J\%, SLT)
\]

\textbf{NEXT} \ J\%

\textbf{FOR} \ J\% = 0 \textbf{TO} \ N\%

\textbf{I\%} = J\% + 1

\begin{align*}
LR\% &= J\% - R\%: \text{IF} \ LR\% < 0 \text{ THEN} \ LR\% = 0 \\
UR\% &= J\% + R\%: \text{IF} \ UR\% > N\% \text{ THEN} \ UR\% = N\%
\end{align*}

\textbf{IF} \ J\% + R\% > N\% \textbf{THEN} 1210

\begin{align*}
STEMP &= STEM + D(J\% + R\%, 1) \\
STEM2 &= STEM2 + D(J\% + R\%, 1) \cdot 2 \\
SSTR &= SSTR + D(J\% + R\%, SLT) \\
STS &= STS + D(J\% + R\%, 1) \cdot D(J\% + R\%, SLT)
\end{align*}

\textbf{1210} \textbf{IF} \ J\% - R\% <= 0 \textbf{THEN} 1260

\begin{align*}
STEMP &= STEM - D(J\% - R\% - 1, 1) \\
STEM2 &= STEM2 - D(J\% - R\% - 1, 1) \cdot 2 \\
SSTR &= SSTR - D(J\% - R\% - 1, SLT) \\
STS &= STS - D(J\% - R\% - 1, 1) \cdot D(J\% - R\% - 1, SLT)
\end{align*}

\textbf{1260} \textbf{IF} \ SLT = 2 \textbf{THEN} TC(I\%) = ((UR\% - LR\% + 1) \cdot STS - SSTR \cdot STEM) / ((UR\% - LR\% + 1) \cdot STEM2 - STEM) \cdot 10000!

\textbf{IF} \ SLT = 3 \textbf{THEN} SC(I\%) = ((UR\% - LR\% + 1) \cdot STS - SSTR \cdot STEM) / ((UR\% - LR\% + 1) \cdot STEM2 - STEM) \cdot 10000!

\textbf{IF} D(J\%, 1) > TMAX \textbf{THEN} TMAX = D(J\%, 1)
\textbf{IF} D(J\%, 1) < TMIN \textbf{THEN} TMIN = D(J\%, 1)

\textbf{IF} \ SLT = 3 \textbf{THEN} 1270

\textbf{IF} \ TC(I\%) > TCMA \textbf{THEN} TCMA = TC(I\%)
\textbf{IF} \ TC(I\%) < TCMI \textbf{THEN} TCMI = TC(I\%)

\textbf{GOTO} 1280

\textbf{1270} \textbf{IF} \ SC(I\%) > SCMA \textbf{THEN} SCMA = SC(I\%)
\textbf{IF} \ SC(I\%) < SCMI \textbf{THEN} SCMI = SC(I\%)

\textbf{1280} \textbf{NEXT} \ J\%

\begin{align*}
XMIN &= 50 \cdot \text{INT}(TMIN / 50) - 50: \text{XMAX} = 50 \cdot \text{INT}(TMAX / 50) + 50 \\
\text{IF} \ SLT = 2 \textbf{THEN} YMIN = 10 \cdot \text{INT}(TCMI / 10) - 10: \text{YMAX} = 10 \cdot \text{INT}(TCMA / 10) + 10 \\
\text{IF} \ SLT = 3 \textbf{THEN} YMIN = .05 \cdot \text{INT}(SCMI / .05) - .05: \text{YMAX} = .05 \cdot \text{INT}(SCMA / .05) + .05
\end{align*}

\textbf{XTIT} = "Temperature (°C)"
\textbf{IF} \ SLT = 2 \textbf{THEN} \text{YTIT} = "tec": \text{YTIT} = "": \text{YUNS} = "(PPM/°C)"
\textbf{IF} \ SLT = 3 \textbf{THEN} \text{YTIT} = "ds/dT": \text{YTIT} = "": \text{YUNS} = "(MPa/°C)"

\textbf{GOSUB} 10000

\textbf{FOR} \ J\% = 0 \textbf{TO} \ N\%

\textbf{I\%} = J\% + 1

\begin{align*}
XPLT &= D(J\%, 1) \\
\text{IF} \ SLT = 2 \textbf{THEN} YPLT &= TC(I\%) \textbf{ELSE} YPLT &= SC(I\%)
\end{align*}

\textbf{GOSUB} 10500

\textbf{NEXT} \ J\%

\textbf{LOCATE} 1, 1

\textbf{PRINT} "Is this acceptable (Y/N)?"

\textbf{1300} \textbf{BS} = \text{INKEYS}: \text{IF} \ BS = "" \textbf{THEN} 1300

\textbf{IF} BS = "Y" \textbf{OR} BS = "y" \textbf{THEN} 1340
\textbf{IF} BS = "N" \textbf{OR} BS = "n" \textbf{THEN} \text{SCREEN} 0: \text{COLOR} 10: \text{RETURN}

\textbf{GOTO} 1300

\textbf{201}
1340 SCREEN 0: COLOR 10
1350 IF SLT = 2 THEN FF2E$ = "DONE"
    IF SLT = 3 THEN FF2S$ = "DONE"
    RETURN
1950 A$ = INKEYS: IF A$ = "" THEN 1950
    RETURN

3000 ********Plot Data*******************
    XX = 2: YY = 5
    CLS
3010 COLOR 2
    LOCATE 7, 10: PRINT "X Axis:": LOCATE 7, 50: PRINT "Y Axis:"
    IF XX = 1 THEN COLOR 4
    LOCATE 9, 13: PRINT "1 - Time": COLOR 2
    IF XX = 2 THEN COLOR 4
    LOCATE 10, 13: PRINT "2 - Temperature": COLOR 2
    IF XX = 3 THEN COLOR 4
    LOCATE 11, 13: PRINT "3 - Strain": COLOR 2

    IF YY = 4 THEN COLOR 4
    LOCATE 9, 53: PRINT "4 - Temperature": COLOR 2
    IF YY = 5 THEN COLOR 4
    LOCATE 10, 53: PRINT "5 - Strain": COLOR 2
    IF YY = 6 THEN COLOR 4
    LOCATE 11, 53: PRINT "6 - Stress": COLOR 2
    IF FF2E$ <> "DONE" THEN COLOR 7
    IF YY = 7 THEN COLOR 4
    LOCATE 12, 53: PRINT "7 - TEC": COLOR 2
    IF FF2S$ <> "DONE" THEN COLOR 7
    IF YY = 8 THEN COLOR 4
    LOCATE 13, 53: PRINT "8 - ds/dT": COLOR 2

3100 PRINT "Type # to change axes, <cr> to accept axes"
3110 A$ = INKEYS: IF A$ = "" THEN 3110
    IF ASC(A$) = 13 THEN 3200
    IF ASC(A$) = 27 THEN RETURN
    A = VAL(A$)
    IF A > 0 AND A < 4 THEN XX = A: GOTO 3010
    IF A > 3 AND A < 7 THEN YY = A: GOTO 3010
    IF A = 7 AND FF2E$ = "DONE" THEN YY = A: GOTO 3010
    IF A = 8 AND FF2S$ = "DONE" THEN YY = A: GOTO 3010
    GOTO 3110

3200 INPUT "Minimum x value:": XMIN
    INPUT "Maximum x value:": XMAX
    INPUT "Minimum y value:": YMIN
    INPUT "Maximum y value:": YMAX

    IF XX = 1 THEN XTITS = "Time (min)"
    IF XX = 2 THEN XTITS = "Temperature (0C)"
    IF XX = 3 THEN XTITS = "Strain (%)"
    IF YY = 4 THEN YTIT1$ = "Temperature": YUN$ = "(0C)"
    IF YY = 5 THEN YTIT1$ = "Strain": YUN$ = "(\%)"
    IF YY = 6 THEN YTIT1$ = "Stress": YUN$ = "(MPa)"

202
IF YY = 7 THEN YTIT1$ = "TEC": YUN$ = "(ppm/°C)"
IF YY = 8 THEN YTIT1$ = "ds/dT": YUN$ = "(MPa/°C)"

GOSUB 10000

FOR I% = 1 TO N%
    XPLOT = D(I%, XX - 1)
    IF YY < 7 THEN YPLOT = D(I%, YY - 3)
    IF YY = 7 THEN YPLOT = TC(I%)
    IF YY = 8 THEN YPLOT = SC(I%)
    GOSUB 10500
NEXT I%

LOCATE 1, 25
PRINT "Hit any key"
3250 A$ = INKEY$: IF A$ = "" THEN 3250
SCREEN 0: COLOR 10
RETURN

7000 '********Change Sample Dimensions**********
IF FF3$ = "CAN'T" THEN RETURN
NL = L: NWI = WI: NTH = TH
7010 CLS
    LOCATE 10, 20: PRINT "Final Sample Length:"; NL
    LOCATE 11, 20: PRINT "Sample Width:"; NWI
    LOCATE 12, 20: PRINT "Sample Thickness:"; NTH
LOCATE 15, 10: PRINT "Are these values OK (Y/N)?"
7050 A$ = INKEY$: IF A$ = "" THEN 7050
    IF A$ = "Y" OR A$ = "y" THEN 7100
    IF A$ <> "N" AND A$ <> "n" THEN 7050
    PRINT : INPUT "New Length (<cr> for no change) (mm): ", NL
    IF NL = 0 THEN LOCATE 17, 38: PRINT L: NL = L
    INPUT "New Width (mm): ", NWI
    IF NWI = 0 THEN LOCATE 18, 38: PRINT WI: NWI = WI
    INPUT "New Thickness (um): ", NTH
    IF NTH = 0 THEN LOCATE 19, 38: PRINT TH: NTH = TH
    GOTO 7010
7100 IF NL <> L AND NWI <> WI AND NTH <> TH THEN RETURN
FOR I% = 1 TO N%
    IF NL = L THEN 7110
        D(I%, 1) = D(I%, 1) * L / NL
    7110 IF NWI = WI AND NTH = TH THEN 7120
        D(I%, 2) = D(I%, 2) * WI * TH / NWI / NTH
7120 NEXT I%
    IF FF2E$="DONE" THEN FF2E$=""
    IF FF2S$="DONE" THEN FF2S$=""
    IF FF6S="DONE" THEN FF6S=""
    L = NL: WI = NWI: TH = NTH
RETURN

10000 '********Setting up Graphics**********
SCREEN 12: CLS
COLOR 14, 1
LFT = 75: BTM = 40: RGT = 20: TOP = 55

203
LINE (LFT - 4, 479 - BTM)-(639 - RGT, 479 - BTM)
FOR I = 1 TO 10
   LINE (INT(I * (640 - RGT - LFT) / 10) + LFT, 479 - BTM + 4)-(INT(I * (640 - RGT - LFT) / 10) + LFT, 479 - BTM - 4)
NEXT I
LOCATE 30, 35: PRINT XTITS$;
LOCATE 29, 6: PRINT USING "#####"; XMIN;
LOCATE 29, 75: PRINT USING "#####"; XMAX;
LINE (LFT, 479 - BTM + 4)-(LFT, 0 + TOP)
FOR I = 1 TO 10
   LINE (LFT - 4, 480 - BTM - INT(I * (480 - TOP - BTM) / 10)-(LFT + 4, 480 - BTM - INT(I * (480 - TOP - BTM) / 10))
NEXT I
LOCATE 14, 1: PRINT YTIT1$; : LOCATE 15, 1: PRINT ytit2$;
LOCATE 28, 2: PRINT USING "#####.#"; YMIN;
LOCATE 4, 2: PRINT USING "#####.#"; YMAX;
RETURN

10500 X = INT((640 - RGT - LFT) / (XMAX - XMIN) * (XPLOT - XMIN)) + LFT
Y = INT((TOP + BTM - 480) / (YMAX - YMIN) * (YPLOT - YMAX)) + TOP
IF 1% = 1 THEN LINE (X, Y)-(X, Y) ELSE LINE -(X, Y)
RETURN

20000 '*****Input Routine**************************************************************************
BS = ""
20010 COLOR 18: PRINT ". ";
20020 A$ = INKEY$: IF A$ = "" THEN 20020
   IF ASC(A$) = 8 AND LEN(B$) > 0 THEN B$ = LEFT$(B$, LEN(B$) - 1): PRINT CHR$(29); " "; CHR$(29); CHR$(29); : GOTO 20050
   IF ASC(A$) = 13 THEN COLOR 2: PRINT CHR$(29); " "; CHR$(29); CHR$(29); : RETURN
   IF ASC(A$) = 27 THEN COLOR 2: PRINT CHR$(29); " "; CHR$(29); CHR$(29); : RETURN
   IF ASC(A$) < 32 THEN 20020
   BS = BS + A$
20040 COLOR 2
   PRINT CHR$(29);
   PRINT A$;
20050 COLOR 2: GOTO 20010
This program curve fits compliance master curves and provides aid in finding the shift function for materials below the glass transition temperature. Unshifted compliance data is obtained from print files with the following format:

\[
\begin{align*}
T_1 \\
\text{t}_{1,1} &<\text{TAB}> D_{1,1} \\
\text{t}_{1,2} &<\text{TAB}> D_{1,2} \\
\text{t}_{1,3} &<\text{TAB}> D_{1,3} \\
&\vdots \\
\text{t}_{1,k(1)} &<\text{TAB}> D_{1,k(1)} \\
&\text{<CR.>} \\
T_2 \\
\text{t}_{2,1} &<\text{TAB}> D_{2,1} \\
\text{t}_{2,2} &<\text{TAB}> D_{2,2} \\
\text{t}_{2,3} &<\text{TAB}> D_{2,3} \\
&\vdots \\
\text{t}_{2,k(2)} &<\text{TAB}> D_{2,k(2)} \\
&\text{<CR.>} \\
&\vdots
\end{align*}
\]

where \(T_j\) are the temperature data, \(t_{ij}\) are the time data, \(D_{ij}\) are the raw compliance data and \(k(j)\) are the number of compliance data points corresponding to \(T_j\). The user is prompted for shift factor values and the raw compliance data is shifted with these values to form a master curve referenced at the first temperature specified in the uploaded data file. The master curve is then fitted with a power law function of the form: \(D(t) = A + Bt^x + Ct^y\).

Curve fitting is performed by minimizing an error function, \(S_r\), defined in terms of the shifted compliance data and the power law fitting function:
The error function can be minimized by setting the derivatives with respect to the fitting coefficients, A, B, C, x and y, equal to zero. Since the derivatives with respect to the exponential coefficients, x and y, result in non-solvable differential equations, derivatives were only taken with respect to A, B and C as shown in equation B.2.

\[
\frac{\partial S_r}{\partial A} = 0 = -2 \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left[ D_{j,i} - A - B \left( \frac{t_{ji}}{a_{T_j}} \right)^x - C \left( \frac{t_{ji}}{a_{T_j}} \right)^y \right]
\]

\[
\frac{\partial S_r}{\partial B} = 0 = -2 \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left[ D_{j,i} - A - B \left( \frac{t_{ji}}{a_{T_j}} \right)^x - C \left( \frac{t_{ji}}{a_{T_j}} \right)^y \right] \left( \frac{t_{ji}}{a_{T_j}} \right)^x
\]

\[
\frac{\partial S_r}{\partial C} = 0 = -2 \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left[ D_{j,i} - A - B \left( \frac{t_{ji}}{a_{T_j}} \right)^x - C \left( \frac{t_{ji}}{a_{T_j}} \right)^y \right] \left( \frac{t_{ji}}{a_{T_j}} \right)^y
\]

The minimized coefficients, A, B and C can then be expressed in terms of the shifted compliance data:

\[
A = \frac{1}{n} \left[ \sum_{j=1}^{m} \sum_{i=1}^{k(j)} D_{j,i} - B \sum_{i=1}^{m} \sum_{j=1}^{k(m)} \left( \frac{t_{ji}}{a_{T_j}} \right)^x - C \sum_{j=1}^{m} \sum_{j=1}^{k(m)} \left( \frac{t_{ji}}{a_{T_j}} \right)^y \right]
\]

\[
B = \frac{D_{T_y} - CT_{xy}}{T_x}
\]

\[
C = \frac{D_{T_x} T_x - DT_{x} T_{xy}}{T_x T_y - T_{xy}^2}
\]

where

\[
S_r = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left[ D_{j,i} - A - B \left( \frac{t_{ji}}{a_{T_j}} \right)^x - C \left( \frac{t_{ji}}{a_{T_j}} \right)^y \right]^2.
\]
\[
T_x = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{2x} - \frac{1}{n} \left[ \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{2x} \right] \\
T_y = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{2y} - \frac{1}{n} \left[ \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{2y} \right] \\
T_{xy} = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{x+y} - \frac{1}{n} \left[ \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{x+y} \right] \\
D_{T_x} = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} D_{j,i} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{x} - \frac{1}{n} \left[ \sum_{j=1}^{m} \sum_{i=1}^{k(j)} D_{j,i} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{x} \right] \\
D_{T_y} = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} D_{j,i} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{y} - \frac{1}{n} \left[ \sum_{j=1}^{m} \sum_{i=1}^{k(j)} D_{j,i} \left( \frac{t_{j,i}}{a_{T,j}} \right)^{y} \right]
\]

and \( n \) is the total number of data points. The fitting coefficients are determined for a range of values for \( x \) and \( y \). The values of \( x \) and \( y \) that produce the lowest error are chosen as the minimized exponential fitting coefficients. A regression coefficient, \( R \), is also calculated as follows:

\[
R = \sqrt{\frac{S_t - S_x}{S_t}} 
\tag{C.4}
\]

where

\[
S_t = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} \left[ D_{j,i} - \left\langle D_{j,i} \right\rangle \right]^2 \quad \text{and} \quad \left\langle D_{j,i} \right\rangle = \sum_{j=1}^{m} \sum_{i=1}^{k(j)} D_{j,i}.
\]
PROGRAM: BESTFIT3.BAS
FINAL VERSION: 4/1/92

DESCRIPTION: THIS PROGRAM CURVE FITS THE COMPLIANCE MASTER CURVE AND PROVIDES AID IN FINDING THE SHIFT FUNCTION FOR MATERIALS BELOW THE GLASS TRANSITION TEMPERATURE. UNSHIFTED COMPLIANCE DATA AT VARIOUS TEMPERATURES IS READ FROM A PRINT FILE THEN SHIFTED WITH USER SPECIFIED SHIFT FACTORS TO FORM A MASTER CURVE REFERENCED AT 30°C. THE MASTER CURVE IS FITTED WITH A POWER LAW FUNCTION OF THE FORM D(T) = A + BT^X + CT^Y AND THE FITTING ERROR IS REPORTED WITH RESPECT TO EACH TEMPERATURE.

NOTE: THE POWER LAW FUNCTION DOES NOT APPLY TO MATERIALS ABOVE THE GLASS TRANSITION TEMPERATURE.

******************************************************

DIM K(20), t(20), LA(20), AA(20), cr(20), TI(20,50), D(20,50), A(30,30), B(30,30)
DIM C(30,30), SR(30,30), CO(8,20)

***INITIAL GUESSES FOR SHIFT FACTORS***
DATA 0,-2.7,-2.8,-3.8,-5.0,-7.5,-9.7,-11.8,-12.7,-13.2,-14.0

**********PARAMETER DEFINITIONS************

STRING VARIABLES:
A$ = GENERAL KEYBOARD INPUT
D$ = DATA INPUT FROM FILE
FS, FO$ = INPUT AND OUTPUT FILENAMES
XTIT$ = X-AXIS TITLE
YTIT1$ = Y-AXIS TITLE #1
YTIT2$ = Y-AXIS TITLE #2
XUN$ = X-AXIS UNITS
YUN$ = Y-AXIS UNITS

INTEGERS:
I%, J%, K%, L%, I% = GENERAL COUNTING
M% = NUMBER OF DIFFERENT TEMPERATURES
N% = TOTAL NUMBER OF DATA POINTS
MK%, ML% = LOCATIONS OF MINIMIZED EXPONENTS

CONSTANTS:
A = GENERAL KEYBOARD INPUT
LT = LOG(TIME)
MA, MB, MC, MX, MY = MINIMIZED POWER LAW COEFFICIENTS
MR = REGRESSION COEFFICIENT
SUMTX = SUMMATION OVER (SHIFTED TIME)^-XX
SUMTY = SUMMATION OVER (SHIFTED TIME)^-YY
SUMT2X = SUMMATION OVER (SHIFTED TIME)^(-2XX)
SUMT2Y = SUMMATION OVER (SHIFTED TIME)^(-2YY)
SUMTXY = SUMMATION OVER (SHIFTED TIME)^(-XX+YY)
SUMD = SUMMATION OVER COMPLIANCE
SUMDXTX = SUMMATION OVER COMPLIANCE TIMES (SHIFTED TIME)^-XX

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SUMDTY = SUMMATION OVER COMPLIANCE TIMES (SHIFTED TIME)^X.YY
SUMERR = FITTING ERROR
SUMERRT = REGRESSION COEFFICIENTS
TX, TY, TXY, DTX, DTY = FUNCTIONS OF SUMS
XX, YY = GUESSES FOR EXPONENTS IN POWER LAW FIT
X, Y = PLOTTING COORDINATES (SCREEN SPACE)
XPLT, YPLT = PLOTTING VALUES
XMIN, XMAX = RANGE SETTINGS FOR X-AXIS
YMIN, YMAX = RANGE SETTINGS FOR Y-AXIS
LFT, RGT = LEFT AND RIGHT PLOT BORDERS
TOP, BTM = UPPER AND LOWER PLOT BORDERS

ARRAYS:
AA(M%) = SHIFT FACTORS
A(K%, L%), B(K%, L%), C(K%, L%) = FITTED COEFFICIENTS FOR EXPONENT GUESSES X AND Y
CO(8, M%) = FUNCTIONS OF SUMS
D(M%, N%) = RAW COMPLIANCE DATA
ER(M%) = FITTING ERRORS AT EACH TEMPERATURE FOR EXPONENTS X AND Y
K(M%) = NUMBER OF DATA POINTS FOR MTH TEMPERATURE
LA(M%) = LOG(SHIFT FACTOR)
MR(M%) = MINIMIZED FITTING ERRORS AT EACH TEMPERATURE
SR(K%, L%) = TOTAL FITTING ERRORS FOR EXPONENTIAL GUESSES X AND Y
T(M%) = TEMPERATURES
TI(M%, N%) = RAW TIME DATA

SCREEN 12: CLS
100 '********Loading File****************************************************
 INPUT "Source Filename: ", FS
105 OPEN "r", 1, FS
  PRINT "Loading data..."
  M% = 0
  N% = 0
160 WHILE NOT EOF(1)
170   I% = 1: FOR II% = 1 TO 2: D$(II%) = ":" : NEXT II%: K% = 1
   INPUT #1, D$
   IF LEN(D$) = 0 THEN 175
   IF (ASC(LEFT$(D$, 1)) > 47 AND ASC(LEFT$(D$, 1)) < 58) OR LEFT$(D$, 1) <> "-"
      THEN 180
175    K(M%) = 1% - 1
    N% = N% + K(M%)
    M% = M% + 1
    I% = 1
    INPUT #1, T(M%)
   GOTO 220
180   IF J% > LEN(D$) THEN 200
    BS = MIDS$(D$(J%, 1))
    IF BS <> CHR$(9) AND BS <> CHR$(32) THEN D$(K%) = D$(K%) + BS: J% = J% + 1: GOTO 180
   IF LEN(D$(K%)) > 0 THEN K% = K% + 1

209
J% = J% + 1: GOTO 180

200   TI(M%, I%) = VAL(D$(1))
      D(M%, I%) = VAL(D$(2))
210   I% = I% + 1
220   WEND
      K(M%) = I% - 1
      N% = N% + K(M%)

250 '**********INPUTING SHIFT FACTORS************************************
      FOR I% = 1 TO M%
          READ LA(I%)
      NEXT I%
      FOR J% = 1 TO M%
          AA(J%) = 10 ^ LA(J%)
      NEXT J%
255   GOSUB 300

257   LOCATE 1, 3: PRINT "A ="; : PRINT USING "#.###^####"; MA
      LOCATE 2, 3: PRINT "B ="; : PRINT USING "#.###^####"; MB
      LOCATE 3, 3: PRINT "C ="; : PRINT USING "#.###^####"; MC
      LOCATE 1, 30: PRINT "x ="; : PRINT USING "#.###"; MX
      LOCATE 2, 30: PRINT "y ="; : PRINT USING "#.##"; MY
      LOCATE 3, 30: PRINT "R ="; : PRINT USING "#.####"; mr
      LOCATE 5, 18: PRINT "Temp:"; : LOCATE 5, 28: PRINT "log(aT)"
      LOCATE 5, 38: PRINT "Error:";
      FOR I% = 1 TO M%
          LOCATE I%+6,13: PRINT "<"; CHRS(I%+96); ">"
          LOCATE I%+6,20: PRINT TI(I%)
          LOCATE I%+6,30: PRINT USING "###.##"; LA(I%)
          LOCATE I%+6,40: PRINT USING "#.###^####"; mr(I%)
      NEXT I%
      LOCATE 26, 20: PRINT "Enter letter to change or <cr> to accept."
260   AS = INKEY$: IF AS = "" THEN 260
      IF AS = "p" OR AS = "P" THEN 255
      IF AS = "s" OR AS = "S" THEN GOSUB 500: GOTO 255
      A = ASC(AS)
      IF A = 13 THEN 600
      IF A > 96 AND A < 98 + M% THEN A = A - 96: GOTO 270
      IF A > 64 AND A < 65 + M% THEN A = A - 64: GOTO 270
      GOTO 260

270   COLOR 2
      FOR I% = 1 TO K(A)
          XPLOT = LOG10(TI(A,I%)/AA(A))
          YPLOT = D(A,I%)
          GOSUB 10500
      NEXT I%: COLOR 14

      LOCATE A + 6, 30
      INPUT ",", AS
      COLOR 0
      FOR I% = 1 TO K(A)
          XPLOT = LOG10(TI(A,I%)/AA(A))
YPLOT = D(A,I%)  
GOSUB 10500  
NEXT I%: COLOR 14  
IF VAL(A$s) <> 0 THEN LA(A) = VAL(A$s)  
FOR J% = 1 TO M%  
  AA(J%) = 10^LA(J%)  
NEXT J%  
LOCATE A + 6, 13: PRINT "<";CHR$(A+96);">
LOCATE A + 6, 20: PRINT T(A)  
LOCATE A + 6, 30: PRINT USING "###.#"; LA(A)  
LOCATE A + 6, 40: PRINT USING "#.##aaaa"; mr(A)  
COLOR 4  
FOR I% = 1 TO K(A)  
  XPLOT = LOG10(TI(A,I%)/AA(A))  
  YPLOT = D(A,I%)  
  GOSUB 10500  
NEXT I%: COLOR 14  
GOTO 260

300 ******Plotting Routine*****************************
XMIN = -1: XMAX = 20  
YMIN = 0  
YMAX = .002  
XTIT$ = "Log(time)"; YTIT2$ = "Comp"; YTIT1$ = "": YUN$ = "(1/MPa)"  
GOSUB 10000  
COLOR 4  
FOR J% = 1 TO M%  
  FOR I% = 1 TO K(M%)  
    IF TI(J%, I%) <= 0 OR AA(J%) <= 0 THEN 350  
    XPLOT = LOG10(TI(J%,I%)/AA(J%))  
    IF XPLOT < XMIN OR XPLOT > XMAX THEN 350  
    YPLOT = D(J%,I%)  
    IF YPLOT < YMIN OR YPLOT > YMAX THEN 350  
    GOSUB 10500  
  NEXT I%  
NEXT J%: COLOR 14  
400 IF MA = 0 THEN 490  
  FOR LT = 0 TO XMAX STEP .1  
    IF LT = 0 THEN I% = 1 ELSE I% = 2  
    XPLOT = LT  
    YPLOT = MA + MB * (10^LT)*MX+MC*(10^LT)^MY  
    IF YPLOT < YMIN OR YPLOT > YMAX THEN 450  
  GOSUB 10500  
450 NEXT LT  
490 RETURN

500 ******Plot Shift Factors*****************************
XMIN = 0: XMAX = 400  
YMIN = INT(LA(M%)) - 1: YMAX = 0  
YTIT2$ = "LOG(aT)"; YUN$ = ""  
GOSUB 10000  
FOR I% = 1 TO M%
XPLOT = T(I%) 
YPLOT = LA(I%) 
X = INT((640 - RGT - LFT) / (XMAX - XMIN) * (XPLOT - XMIN)) + LFT 
Y = INT((TOP + BTM - 480) / (YMAX - YMIN) * (YPLOT - YMAX)) + TOP 
LINE (X - 5, Y) - (X + 5, Y) 
LINE (X, Y - 5) - (X, Y + 5) 

NEXT I%

510 A$ = INKEY$: IF A$ = "" THEN 510 
RETURN 

600 '********MAIN PROGRAM*******************************
  FOR J% = 1 TO M% 
    AA(J%) = 10 ^ LA(J%) 
  NEXT J%
  GOSUB 1000 
  GOSUB 400 
  GOTO 257 

700 '********CALCULATING COEFFICIENTS**************************
  FOR J% = 1 TO M% 
    FOR KK% = 1 TO 8 
      CO(KK%, J%) = 0 
    NEXT KK%
    FOR I% = 1 TO K(J%) 
      CO(1, J%) = CO(1, J%) + T(J%, I%) ^ XX 
      CO(2, J%) = CO(2, J%) + T(J%, I%) ^ YY 
      CO(3, J%) = CO(3, J%) + D(J%, I%) 
      CO(4, J%) = CO(4, J%) + T(J%, I%) ^ 2 * XX 
      CO(5, J%) = CO(5, J%) + T(J%, I%) ^ (XX + YY) 
      CO(6, J%) = CO(6, J%) + D(J%, I%) ^ T(J%, I%) ^ XX 
      CO(7, J%) = CO(7, J%) + D(J%, I%) ^ T(J%, I%) ^ YY 
      CO(8, J%) = CO(8, J%) + T(I%, I%) ^ (2 * YY) 
    NEXT I%
  NEXT J%
RETURN

1000 '********REGRESSIONS*******************************
  MER = -1E+38: MX = 0: MY = 0 
  K% = 1 
  FOR XX = .05 TO .05 STEP .01 
    LOCATE 1, 60: PRINT K%, 
    L% = 1 
    FOR YY = .64 TO .64 STEP .01 
      LOCATE 1, 65 
      PRINT L% 
      SUMERR = 0 
      SUMERRT = 0 
      GOSUB 700 
      SUMTX = 0 
      SUMTY = 0 
      SUMT2X = 0 
      SUMT2Y = 0 
      SUMTXY = 0 
      SUMD = 0
SUMDTX = 0
SUMDTY = 0
FOR J% = 1 TO M%
    SUMTX = SUMTX + CO(1, J%) * AA(J%) \(\cdot xx\)
    SUMTY = SUMTY + CO(2, J%) * AA(J%) \(\cdot yy\)
    SUMT2X = SUMT2X + CO(4, J%) * AA(J%) \(\cdot (2 \cdot xx)\)
    SUMT2Y = SUMT2Y + CO(8, J%) * AA(J%) \(\cdot (2 \cdot yy)\)
    SUMTXY = SUMTXY + CO(5, J%) * AA(J%) \(\cdot (x \cdot yy)\)
    SUMD = SUMD + CO(3, J%)
    SUMDTX = SUMDTX + CO(6, J%) * AA(J%) \(\cdot xx\)
    SUMDTY = SUMDTY + CO(7, J%) * AA(J%) \(\cdot yy\)
NEXT J%

TX = SUMT2X - SUMTX \(\cdot 2 / N%\)
TY = SUMT2Y - SUMTY \(\cdot 2 / N%\)
TXY = SUMTXY - SUMTX \(\cdot SUMTY / N%\)
DTX = SUMDTX - SUMD \(\cdot SUMTX / N%\)
DTY = SUMDTY - SUMD \(\cdot SUMTY / N%\)
C(K%, L%) = (DTY \(\cdot TX - DTX \cdot TXY\)) / (TX \(\cdot TY - TXY \cdot 2\))
B(K%, L%) = (DTX - C(K%, L%) \(\cdot TXY\)) / TX
A(K%, L%) = (SUMD - B(K%, L%) \(\cdot SUMTX - C(K%, L%) \cdot SUMTY\)) / N%
FOR J% = 1 TO M%
    ER(J%) = 0
    FOR I% = 1 TO K(J%)
        D = A(K%, L%) + B(K%, L%) \(\cdot (TI(J%, I%) / AA(J%)) \cdot xx\) + C(K%, L%) \(\cdot (TI(J%, I%) / AA(J%)) \cdot yy\)
    SUMERR = SUMERR + (D(J%, I%) - D) \(\cdot 2\)
    SUMERRT = SUMERRT + (D(J%, I%) - SUMD / N%) \(\cdot 2\)
    ER(J%) = ER(J%) + (D(J%, I%) - D) \(\cdot 2\)
NEXT I%
NEXT J%
SR(K%, L%) = ((SUMERRT - SUMERR) / SUMERRT) \(\cdot 5\)
IF SR(K%, L%) > MR THEN MR = SR(K%, L%): MK% = K%: ML% = L%: MX = X:
MY = Y: FOR J% = 1 TO M%: MR(J%) = ER(J%): NEXT J%
L% = L% + 1
NEXT YY
K% = K% + 1
NEXT XX

MA = A(MK%, ML%)
MB = B(MK%, ML%)
MC = C(MK%, ML%)

RETURN

10000 ****** Setting up Graphics**********************************************************
SCREEN 12: CLS
COLOR 14, 1
LFT = 75: BTM = 40: RGT = 20: TOP = 55
LINE (LFT - 4, 479 - BTM)-(639 - RGT, 479 - BTM)
FOR I = 1 TO 10
    LINE (INT(I \(\cdot (640 - RGT - LFT) / 10\) + LFT, 479 - BTM + 4)-(INT(I \(\cdot (640 - RGT - LFT) / 10\) + LFT, 479 - BTM - 4)
NEXT I
LOCATE 30, 35: PRINT XTITS;
LOCATE 29, 10: PRINT USING "#####.#"; XMIN;
LOCATE 29, 74: PRINT USING "#####.#"; XMAX;
LINE (LFT, 479 - BTM + 4)-(LFT, 0 + TOP)
FOR I = 1 TO 10
    LINE (LFT - 4, 480 - BTM - INT(I * (480 - TOP - BTM) / 10))-(LFT + 4, 480 - BTM - INT(I * (480 - TOP - BTM) / 10))
NEXT I
LOCATE 14, 1: PRINT YTIT1$; : LOCATE 15, 1: PRINT YTIT2$;
LOCATE 16, 1: PRINT YUN$;
LOCATE 28, 2: PRINT USING "#####.#"; YMIN;
LOCATE 4, 2: PRINT USING "#####.#", YMAX;
RETURN

10500 X = INT((640 - RGT - LFT) / (XMAX - XMIN)) * (XPLOT - XMIN) + LFT
Y = INT((TOP + BTM - 480) / (YMAX - YMIN)) * (YPLOT - YMIN) + TOP
IF I% = 1 THEN LINE (X, Y)-(X, Y) ELSE LINE -(X, Y)
RETURN
APPENDIX D

SOURCE CODE LISTING FOR FARTFC1.BAS

This program determines a time-dependent modulus master curve, \( E(t) \), with knowledge of the time-dependent compliance master curve, \( D(t) \). The compliance is expressed in terms of an exponential series defined as follows:

\[
D(t) = D_0 + D_1(1 - e^{-\tau_1}) + D_2(1 - e^{-\tau_2}) + \ldots + D_n(1 - e^{-\tau_n}) \quad (D.1)
\]

where \( D_i \) and \( \tau_i \) are known coefficients. The moduli master curves could be found from the compliance master curves through the relationship \( \bar{D}(s)\bar{E}(s) = 1/s^2 \) where \( \bar{D} \) and \( \bar{E} \) are the Laplace transforms of the compliance and modulus master curves respectively and \( s \) is the variable in Laplace space. The Laplace transform of equation \( D.1 \) is:

\[
\bar{D}(s) = \frac{1}{s} \sum_{i=0}^{n} D_i \left( \frac{1}{s + 1/\tau_i} \right) = \frac{D_1}{(s + 1/\tau_1)} - \frac{D_2}{(s + 1/\tau_2)} - \ldots - \frac{D_n}{(s + 1/\tau_n)} \quad (D.2)
\]

and the transform of the modulus becomes:

\[
\bar{E}(s) = \left( \sum_{i=0}^{n} \frac{s^2D_i}{(s + 1/\tau_i)} \right) = \frac{s^2D_1}{(s + 1/\tau_1)} - \frac{s^2D_2}{(s + 1/\tau_2)} - \ldots - \frac{s^2D_n}{(s + 1/\tau_n)} \quad (D.3)
\]

When equation \( D.3 \) is broken up into partial fractions, \( \bar{E}(s) \) can be expressed in a form more amenable to finding an inverse Laplace transform:

\[
\bar{E}(s) = \frac{1}{D_0} \left( \frac{C_0}{s} + \frac{C_1}{s-R_1} + \frac{C_2}{s-R_2} + \ldots + \frac{C_n}{s-R_n} \right) \quad (D.4)
\]

where \( C_i \) and \( R_i \) are calculated coefficients from the partial fractions procedure. Taking the inverse Laplace transform, the master curve for the time-dependent modulus is:

\[
E(t) = E_0 + E_1e^{-\tau_1} + E_2e^{-\tau_2} + \ldots + E_ne^{-\tau_n} \quad (D.5)
\]
where \( E_i = C_i / D_0 \), \( \tau'_i = -1 / R_i \) and \( \sum_{i=1}^{n} C_i = 1 \).

Coefficients for the time-dependent compliance are specified within the program and the coefficients for the time-dependent modulus are calculated using the partial fraction procedure.

```
* PROGRAM: PARTFRC1.BAS
* FINAL VERSION: 4/12/92
* WRITTEN BY: ROBERT JENNINGS

* DESCRIPTION: THIS PROGRAM DETERMINES A TIME-DEPENDENT MODULUS MASTER CURVE, \( E(T) \), WITH KNOWLEDGE OF THE TIME-DEPENDENT COMPLIANCE MASTER CURVE, \( D(T) \). THE COMPLIANCE IS EXPRESSED IN TERMS OF AN EXPONENTIAL SERIES. THE LAPLACE TRANSFORMED MODULUS IS THEN FOUND IN TERMS OF THE LAPLACE TRANSFORMED COMPLIANCE. A PARTIAL FRACTIONS ROUTINE IS USED IN THIS PROGRAM TO EXPRESS THE MODULUS IN A FORM AMENABLE TO TAKING THE INVERSE LAPLACE TRANSFORM. THE COEFFICIENTS OF THE EXPONENTIAL SERIES REPRESENTING THE TIME-DEPENDENT MODULUS ARE THEN OUTPUTTED.

* NOTE: THIS PROGRAM CAN ONLY HANDLE RELAXATION TIME RANGES BETWEEN 1 AND \( 10^{20} \) SECONDS. WHEN TIMES IN EXCESS OF THIS RANGE ARE USED, ROUND-OFF ERROR BECOMES TOO LARGE PRODUCING INACCURATE RESULTS. IT IS POSSIBLE TO SPLIT THE MASTER CURVE UP INTO TWO OR MORE SMALLER TIME RANGES WITH LARGE OVERLAPS THEN IGNORE THE RESULTS CALCULATED AT THE EDGES OF THE SMALLER TIME RANGES.

* DIM R#(30),D#(30),N#(30),C#(30),E#(30),DN#(30),T#(30),TA#(30),P#(30)

**********PARAMETER DEFINITIONS**********

' STRING VARIABLES:
   FOS$ = OUTPUT FILENAME

' INTEGERS:
   I%,J%,K% = GENERAL COUNTING
   N% = NUMBER OF COEFFICIENTS

' CONSTANTS:
   TA=DUMMY RELAXATION TIME
```
HIGH DEFINITION CONSTANTS:

ER# = ERROR ALLOWANCE FOR ROOT DETERMINATION
LS# = LOG(S#)
S# = LAPLACE VARIABLE
SU#,SL# = UPPER AND LOWER BOUNDS IN ROOT DETERMINATIONS
P# = POLYNOMIAL VALUE FOR S#
PU#,PL# = UPPER AND LOWER POLYNOMIAL BOUNDS FOR SU# AND SL#
OS#,OP# = OLD S# AND P# VALUES
SUM# = SUM OVER UNNORMALIZED PARTIAL FRACTION COEFFICIENTS
SUMD# = SUM OVER COMPLIANCE COEFFICIENTS

ARRAYS:

C#(N%) = PARTIAL FRACTION COEFFICIENTS
D#(N%) = COMPLIANCE COEFFICIENTS
E#(N%) = MODULUS COEFFICIENTS
N#(N%),DN(N%) = COEFFICIENTS FOR DETERMINING PARTIAL FRACTION
     COEFFICIENTS
P#(N%) = DENOMINATOR POLYNOMIALS
R#(N%) = ROOTS TO DENOMINATOR POLYNOMIAL
         = -1/MODULUS RELAX. TIMES
T#(N%) = 1/COMPLIANCE RELAXATION TIMES

*******************************************************************************

CLS
INPUT"Output Filename: ",fo$
OPEN"O",#2,FOS$

N%=21
ER#=.0000001
T#(0)=0
T#(1)=1
T#(2)=1E-2
T#(3)=1E-4
T#(4)=1E-6
T#(5)=1E-8
T#(6)=1E-10
T#(7)=1E-12
T#(8)=1E-14
T#(9)=1E-16
T#(10)=1E-18
T#(11)=1E-20
T#(12)=1E-22
T#(13)=1E-24
T#(14)=1E-26
T#(15)=1E-28
T#(16)=1E-30
T#(17)=1E-32
T#(18)=1E-34
T#(19)=1E-36
T#(20)=1E-38
T#(21)=1E-40
D#(0)=3.15E-4
D#(1)=2.5E-5
D#(2)=2.65E-5
D#(3)=2.8E-5
D#(4)=3E-5
D#(5)=3.4E-5
D#(6)=3.8E-5
D#(7)=5E-5
D#(8)=8E-5
D#(9)=2E-4
D#(10)=6E-4
D#(11)=1.6E-3
D#(12)=4E-3
D#(13)=5.3E-3
D#(14)=5.5E-3
D#(15)=5.7E-3
D#(16)=5.8E-3
D#(17)=6E-3
D#(18)=6.6E-3
D#(19)=8.4E-3
D#(20)=9.2E-3
D#(21)=1E-2

FOR I%=0 TO N%
    SUMD#=SUMD#+D#(I%)
NEXT I%

K%=1:R#(0)=0

'********FINDING ROOTS OF DENOMINATOR POLYNOMIAL***********************
FOR LS#=1 TO -20 STEP -.1
    S#=-10^LS#
    GOSUB 100
    IF LS#=1 THEN SU#=S#:PU#=P#:GOTO 5
    IF SGN(P#)=SGN(OP#) THEN 5
    SL#=OS#:SU#=S#:PL#=OP#:PU#=P#
4   S#=(SL#+SU#)/2
    GOSUB 100
    IF ABS((SL#-SU#)/S#)<ER# THEN GOSUB 200:GOTO 5
    IF SGN(P#)=SGN(PL#) THEN SL#=S# ELSE SU#=S#
    GOTO 4
5   OS#=SU#
    OP#=PU#
NEXT LS#

'********FINDING PARTIAL FRACTION COEFFICIENTS*****************************
FOR I%=0 TO N%
    N#(I%)=1
    DN#(I%)=1
    FOR J%=0 TO N%
        IF J%=0 THEN 10
        TA=1/EXP10(J%-1)
        N#(I%)=N#(I%)*(R#(I%)+TA)
    10   IF I%=J% THEN 20
DN/(1%) = DN/(1%) * (R#/1% - R#/1%))

NEXT J%
C#/1% = N#/1% / DN#/1%
SUM# = SUM# + C#/1%

NEXT I%

'*'********CALCULATING MODULUS COEFFICIENTS'**************************************
FOR 1% = 0 TO N%
E#/1% = C#/1% / SUM#/D#/0)
SUME# = SUME# + E#/1%)
NEXT I%

'*'********OUTPUT RESULTS'*******************************************************
?"I", "Relaxation Times", "Costants"
?#2,"i%",CHR$(9);"i(i)%;CHR$(9);"D(i)%;CHR$(9);"t(i)%;CHR$(9);"E(i)%
FOR I% = 0 TO N%
IF I% = 0 THEN ?%",c#(i%);?#2,i%;CHR$(9);D#(I%);CHR$(9);CHR$(9);E#(i%):goto 30
?%",-1/R#/1%),E#(1%)
?#2,1%;CHR$(9);T#/1%;CHR$(9);D#(I%);CHR$(9);E#(1%)

NEXT I%

CLOSE#2
END

100 '********CALCULATING DENOMINATOR POLYNOMIAL FOR S#**************
FOR I% = 0 TO N%
P#/1% = 1
FOR J% = 1 TO N%
IF J% = I% THEN 105
P#/1% = P#/1% * (S# + T#/1%))
105 NEXT J%
IF I% = 0 THEN P#/1% = P#/1% * SUMD#: GOTO 107
P#/1% = P#/1% * D#/1% * S#
107 NEXT I%

P# = P#(0)
FOR I% = 1 TO N%
P# = P# - P#/1%
NEXT I%

RETURN

200 '******RECORD ROOT AND PRINT BOUNDS'***************************************
R#/K%# = S#
S# = SL#: GOSUB 100; PL# = P#
S# = SU#: GOSUB 100; PU# = P#
?K%,SL#,SU#
?,PL#,PU#
K% = K% + 1
?:?:?
RETURN

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APPENDIX E
SOURCE CODE LISTING FOR THRMD9.BAS

This program simulates the response of a linear viscoelastic material to various stress and thermal histories. The time and temperature dependent mechanical and thermal properties are specified within the program in the form of analytical equations. The user also specifies the temperature and mechanical history to be imposed and the response of the material is calculated using linear viscoelastic convolution integrals.

The program has also been designed to consider inherent temperature effects (vertical shifting) in the mechanical properties if specified. The constitutive equations used in this case are a slightly modified version of the viscoelastic equations discussed in Chapter III. The constitutive equations used in this program are listed below:

\[
\sigma(t) = \bar{\sigma}(\xi) = \left( \int_{T_0}^{T(\xi)} E_R(T) dT \right) \left( \int_0^\xi E(\xi' - \xi) \frac{\partial}{\partial \xi'} [\bar{\varepsilon}(\xi') - \bar{\varepsilon}^0(\xi')] d\xi' \right)
\]

\[
\varepsilon(t) = \bar{\varepsilon}(\xi) = \bar{\varepsilon}^0(\xi) + \left( \int_{T_0}^{T(\xi)} D_R(T) dT \right) \left( \int_0^\xi D(\xi' - \xi) \frac{\partial \bar{\sigma}(\xi')}{\partial \xi'} d\xi' \right)
\]

\[
\bar{\varepsilon}^0(\xi) = \int_{T_0}^{T(\xi)} \alpha(T) dT
\]

where:
\[
\xi = \int_{-\infty}^{\tau} \frac{1}{a_T[T(\eta)]} d\eta \\
\tau \leq t, \\
0 \leq \tau \leq t.
\]

and \(D_R\) and \(E_R\) are the relative temperature dependent contributions to the compliance and modulus. This form of temperature dependence was chosen to be consistent with incremental elasticity.

All integrations in this program are performed using the trapezoidal rule. For best results 20 to 50 calculation segments per stage is sufficient.
A$ = GENERAL KEYBOARD INPUT
FS = OUTPUT FILENAME
XTITS$ = X-AXIS TITLE
YTIT1$ = Y-AXIS TITLE #1
YTIT2$ = Y-AXIS TITLE #2
XUN$,YUN$ = UNITS FOR X AND Y-AXES

'INTEGERS:
I%,II%,J%,K% = GENERAL COUNTING
IP% = PLOTTING FLAG
N% = TOTAL # POINTS
NP% = # CALCULATION POINTS PER STAGE
NS% = # STAGES

'CONSTANTS:
AA,AE,AD,AK = THERMAL EXPANSION PARAMETERS
DA,DB,DC,DN,DM = TIME DEPENDENT COMPLIANCE PARAMETERS
MA,MB,MC,MN,MM = TIME DEPENDENT MODULUS PARAMETERS
KA,KB = SHIFT FACTOR PARAMETERS
FD1,FD2 = COMPLIANCES
FM1,FM2 = MODULI
T = TEMPERATURE
R = HEATING + COOLING RATE
X,Y = PLOTTING COORDINATES (SCREEN SPACE)
XPLLOT,YPLOT = PLOTTING VALUES
XMIN,XMAX = RANGE SETTINGS FOR X-AXIS PLOT
YMIN,YMAX = RANGE SETTINGS FOR Y-AXIS PLOT
LFT,JRT = LEFT AND RIGHT PLOT BORDERS
BTM,TOP = BOTTOM AND TOP PLOT BORDERS

'HIGH DEFINITION CONSTANTS:
DX1#,DX2# = DELTA REDUCED TIME

'ARRAYS:
DT(N%) = REDUCED TIME DERIVATIVE TEMPERATURE
DS(N%) = REDUCED TIME DERIVATIVE STRESS
DE(N%) = REDUCED TIME DERIVATIVE STRAIN
S(N%) = STRESS
E(N%) = TOTAL STRAIN
I%(NS%) = STAGE MARKERS
R(NS%) = HEATING RATES
T(N%) = TEMPERATURE
TEMP(NS%) = TEMPERATURE BOUNDARIES FOR EACH STAGE
TI(N%) = TIME
STRAIN(NS%) = STRAIN BOUNDARIES FOR EACH STAGE
STRESS(NS%) = STRESS BOUNDARIES FOR EACH STAGE
X#(N%) = REDUCED TIME
MCS(NS%) = MECHANICAL CONTROL MARKER

FUNCTIONS
FNA(T) = STRAIN DUE TO THERMAL EXPANSION
FNTEC(T) = THERMAL EXPANSION COEFFICIENT
FNAT(r) = SHIFT FUNCTION
FND(X) = TIME-DEPENDENT COMPLIANCE
FNDR(X) = TEMPERATURE DEPENDENT RELATIVE COMPLIANCE
FNADR(X) = AVERAGE OF TEMPERATURE DEPENDENT RELATIVE COMPLIANCE
FNAM(R)(X) = TIME-DEPENDENT MODULUS
FNMR(X) = TEMPERATURE DEPENDENT RELATIVE MODULUS
FNAMR(X) = AVERAGE OF TEMPERATURE DEPENDENT RELATIVE MODULUS

***COMPLIANCE***
DA=2.538E-4
DB=9.303E-5
DC=3.289E-15
DN=.05
DM=.64

DEF FND(X) = DA+DB*X^DN+DC*X^DM
DEF FNDR(T) = 1
DEF FNADR(T) = 1

***MODULUS***
MA=2.538E-4
MB=9.303E-5
MC=3.289E-15
MN=.05
MM=.64

DEF FNM(X) = 1/(MA+MB*X^MN+MC*X^MM)
DEF FNMR(T) = 1
DEF FNAMR(T) = 1

***THERMAL EXPANSION***
AA=28E-6
AE=3000
AK=2850
AD=5

DEF FNTEC(T) = AA*AK/(AE-AD*T)
DEF FNA(T) = -AA*AK/AD*LOG((AE-AD*T)/(AE-AD*30))*100

***SHIFT FUNCTION***
KA = .3980
KB = .03892

DEF FNAT(T) = 10^(KA+KB*T)

***CALCULATION PARAMETERS***
NP% = 50
NS% = 6
FOR I%=0 TO NS%
   I%(I%) = I%*50
NEXT I%

N%=I%(NS%)
CLS
INPUT"OUTPUT FILENAME: ",FS
OPEN"O",#2,FS

10 '********SET UP GRAPH********
XTIT$="TEMP":XMIN=0:XMAX=400
YTIT1$="STRAIN":YTIT2$="(%)":YMIN=0:YMAX=1.4
GOSUB 10000

50 '********ESTABLISHING MECHANICAL HISTORY********
'NOTE: BEGINING AND END POINTS OF CYCLE LEGS ARE DEFINED HERE
' STRAIN=0 MEANS ISOSTRAIN
' STRESS=0 MEANS ISOSTRESS UNDER NO STRESS

STRESS(0)=0:STRAIN(0)=0
MCS(1)="STRESS":STRESS(1)=0:STRAIN(1)=0
MCS(2)="STRAIN":STRESS(2)=0:STRAIN(2)=0
MCS(3)="STRESS":STRESS(3)=0:STRAIN(3)=0
MCS(4)="STRESS":STRESS(4)=0:STRAIN(4)=0
MCS(5)="STRESS":STRESS(5)=0:STRAIN(5)=0
MCS(6)="STRESS":STRESS(6)=0:STRAIN(6)=0
MCS(7)="STRESS":STRESS(7)=0:STRAIN(7)=0
MCS(8)="STRESS":STRESS(8)=0:STRAIN(8)=0

100 '********ESTABLISHING THERMAL HISTORY********

TEMP(0) = 30
TEMP(1) = 300
TEMP(2) = 30
TEMP(3) = 100
TEMP(4) = 30
TEMP(5) = 350
TEMP(6) = 30
TEMP(7) = 350
TEMP(8) = 30

'NOTE: DURING ISOTHERMAL LEG, R MEANS LEG TIME

R=5
FOR I%=1 TO NS%
  R(I%)=R
NEXT I%

T(0)=TEMP(0)
TI(0)=0
FOR I%=1 TO NS%
  IF TEMP(J%)=TEMP(J%-1) THEN 120
  FOR I%=I%(J%-1)+1 TO I%(J%)
    T(I%)=TEMP(J%-1)+(I%-I%(J%-1))*(TEMP(J%)-TEMP(J%-1))/(I%(J%)-I%(J%-1))
    TI(I%)=TI(I%(J%-1))+ABS(T(I%)-TEMP(J%-1))/R(J%)*60
  NEXT I%
  GOTO 130
120 FOR I%=I%(J%-1)+1 TO I%(J%)

224
$T(I%) = TEMP(J%-1)$

$TI(I%) = TI(I%(J%-1)) + (I%-I%(J%-1))(I%(J%-1)-1)$

NEXT I%

130 NEXT J%

150 '**********CALCULATE REDUCED TIME SCALE**********************

$X#(0) = 0$

FOR I%=1 TO I%(NS%)

$X#(I%) = X#(I%-1) + (FNAT(T(I%)) + FNAT(T(I%(J%-1)))) * (TI(I%) - TI(I%-1))/2$

NEXT I%

200 '**********CALCULATE TEMPERATURE DERIVATIVES**********************

$DT(0) = (T(1) - T(0))/(X#(1) - X#(0))$

FOR I%=1 TO I%(NS%)

$DT(I%) = (T(I%) - T(I%-1))/(X#(I%) - X#(I%-1))$

NEXT I%

300 '****CALCULATING CONVOLUTION INTEGRALS*******************************

IP%=1

E(0)=0: S(0)=STRESS(0)

XPLOT=T(0)

YPLOT=E(0)

GOSUB 10500

IP%=0

FOR II%=1 TO NS%

IF MCS(II%)="STRAIN" THEN 350

FOR I%=I%(II%-1)+1 TO I%(II%)

$S(I%) = STRESS(II%-1) + (I%-1(I%-1))/((I%(II%-1) - I%(II%-1)))*STRESS(II%)-STRESS(II%-1))$

NEXT I%

FOR I%=I%(II%-1)+1 TO I%(II%)

$DS(I%) = (S(I%) - S(I%-1))/(X#(I%) - X#(I%-1))$

NEXT I%

FOR I%=I%(II%-1)+1 TO I%(II%)

FOR J%=1 TO 1%

$DX1# = X#(I%) - X#(J%)$

FD1=FND(DX1#)

$DX2# = X#(I%) - X#(J%-1)$

FD2=FND(DX2#)

$E(I%) = E(I%) + (FD1*DS(J%)+FD2*DS(J%))*X#(J%)/2*100$

NEXT J%

E(I%) = E(I%)*FNADR(T(I%)) + FNA(T(I%))

XPLOT = T(I%)

YPLOT = E(I%)

GOSUB 10500

IP%=0

LOCATE 1,70: ?I%

NEXT I%

GOTO 400

350 FOR I%=I%(II%-1)+1 TO I%(II%)

IF STRAIN(II%)=0 THEN E(I%) = E(I%(II%-1)): GOTO 360
E(I%) = FNA(T(I%)) + STRAIN(I%-1) + (I%-1)(II%-1)/(I%)(II%-1)
DE(I%) = ((E(I%) - FNA(T(I%))) - (E(I%-1) - FNA(T(I%-1))))/(X#(I%) - X#(I%-1))

FOR I%=I%(II%-1) + 1 TO I%(II%)
   FOR J%=1 TO 1%
      DX1# = X#(I%) - X#(J%)
      FM1 = FNM(DX1#)
      DX2# = X#(I%) - X#(J%-1)
      FM2 = FNM(DX2#)
      S(I%) = S(I%) + (FM1*DE(J%)/100 + FM2*DE(J%)/100)*(X#(J%) - X#(J%-1))/2
   NEXT J%
   S(I%) = FNM(F(T(I%)))*S(I%)
   XPLOT = T(I%)
   YPLOT = E(I%)
   GOSUB 10500
   LOCATE 1,70: ?I%
   LOCATE 2,62: "Stress:"; ?USING "###.##"; S(I%)
NEXT I%

FOR I%=I%(II%-1) + 1 TO I%(II%)
   DS(I%) = (S(I%) - S(I%-1))/(X#(I%) - X#(I%-1))
NEXT I%

END

2000 "********SAVING DATA***************************************************
LOCATE 1,1
?"SAVING DATA"
?#2,"Heating Rates (°C/min):"
FOR J%=1 TO NS%
   ?#2,"Stage #"J%"":"; CHR$(9); R(J%)
NEXT J%
?#2,""
?#2,"Time":CHR$(9); "Red.Time":CHR$(9); "Temp":CHR$(9); "Strain":
?#2,CHR$(9); "Stress"
?#2, (sec);CHR$(9); " (sec)";CHR$(9); " (°C)";CHR$(9); " (%)"
?#2,CHR$(9); " (MPa)"
?#2,"
FOR I%=0 TO I%(NS%)
   ?#2,TI(I%);CHR$(9);X#/I%;CHR$(9);T(I%);CHR$(9);E(I%);CHR$(9);
   ?#2,S(I%)
NEXT I%
CLOSE #2

?"ALL DONE"
END

10000 "********SETTING UP GRAPHICS*****************************************************************************
SCREEN 12:CLS
COLOR 14, 1
LFT = 75: BTM = 40: RGT = 20: TOP = 55
LINE(LFT-4,479-BTM)-(639-RGT,479-BTM)
FOR I = 1 TO 10
LINE (INT(I*(640-RGT-LFT)/10)+LFT,479-BTM+4)-(INT(I*(640-RGT-LFT)/10)+LFT,479-BTM-4)
NEXT I
LOCATE 30,35: PRINT XTIT$;
LOCATE 29,6: PRINT USING"####.#";XMIN;
LOCATE 29,75:PRINT USING"####.#";XMAX;
LINE (LFT,479-BTM+4)-(LFT,0+TOP)
FOR I = 1 TO 10
   LINE(LFT-4,480-BTM-INT(I*(480-TOP-BTM)/10))-(LFT+4,480-BTM-INT(I*(480-TOP-BTM)/10))
NEXT I
LOCATE 14,1:PRINT YTIT1$;
LOCATE 15,1:PRINT YTIT2$;
LOCATE 16,1:?YUNS;
LOCATE 28,2:PRINT USING"####.#";YMIN;
LOCATE 4,2:PRINT USING"####.#";YMAX;
RETURN

10500 X = INT((640-RGT-LFT)/(XMAX-XMIN)*(XPLOT-XMIN))+LFT
Y = INT((TOP+BTM-480)/(YMAX-YMIN)*(YPLOT-YMAX))+TOP
IF IP% = 1 THEN LINE (X, Y)-(X, Y) ELSE LINE -(X, Y)
RETURN


Edman, J.R., Coburn, J.C., and Pottiger, M., To be Published.


Kratky, O., "Zum Deformationsmechanismus der Faserstoffe, I.", Kolloid Z., 64, 213 (1933).


Upilex Material Property Sheet, Ube Industries, LTD. (1986).


