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THERMOPLASTIC ELASTOMERS AS LOVA (LOW VULNERABILITY
AMMUNITION) BINDERS(U) MASSACHUSETTS UNIV AMHERST DEPT
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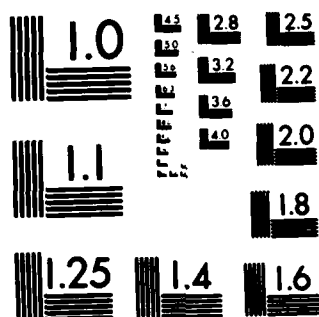
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OFFICE OF NAVAL RESEARCH

Task # NR 659-795

Contract # N00014-83-K-0083

TECHNICAL REPORT NO. 1

Annual Report on Thermoplastic Elastomers as LOVA Binders

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December 1, 1983

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1. INTRODUCTION - LOVA POLYMERS

The project seeks to synthesize and test polymers for application as binders in ammunition charges such that the vulnerability of the explosive to premature or extraneous detonation will be lowered (Low Vulnerability Ammunition = LOVA).

The desired properties for such a binder are:

Low T_g ($< -60^\circ\text{C}$)

Moderate stress at 400% strain

Long term oxidative stability (up to 80°C)

Bonding to cyclic nitramine pellets

High density (> 1.15)

Endothermic decomposition ($200 - 250^\circ\text{C}$)

Acid or thermal initiated endothermic decomposition ($200 - 250^\circ\text{C}$)

The latter two properties are special aspects of LOVA binders.

The University of Massachusetts effort aims at synthesis, mechanical testing, and processing aspects of development of an optimal LOVA binder. The primary approach is to synthesize thermoplastic elastomers (TPE). These are elastomeric by virtue of the soft blocks being crosslinked by crystalline hard blocks. Melting the hard block renders the polymer processible, but reformation of the crosslinks at ambient temperature restores elasticity. Synthesis of a variety of TPE's with hard and soft segments of a range of lengths and identities, adjustments of synthesis based on extensive mechanical tests, and development processing procedures for the highly filled TPE's constitutes the project. The desire is to converge on the above listed properties.

2. LOVA POLYMER SYNTHESIS

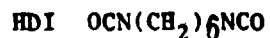
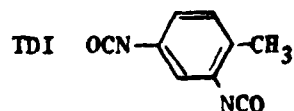
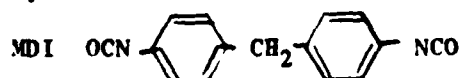
I. Current Status

Synthesis of a series of segmented polyether polyurethane (PEPU) and polyether polyimide (PEPI) copolymers has been completed. New copolymers are being designed based upon the thermal, mechanical, and rheological properties observed for the initial series and to test some fundamental ideas about structure property relationships in these materials.

II. PEPU Copolymers

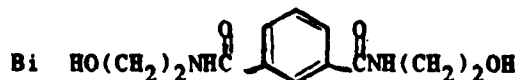
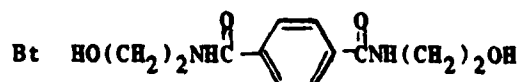
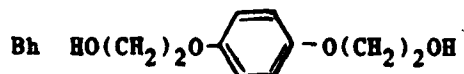
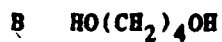
Polymers have been synthesized using poly(propylene oxide) $\bar{M} = 2000$ or 4000 as soft segment and polyurethane hard segments based on the following diisocyanates and chain extenders.

Diisocyanates:



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Chain Extenders:

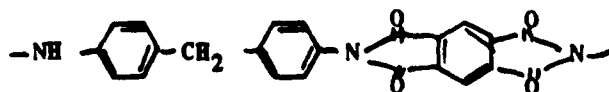


Lists of the polymers synthesized are given in Tables 2.1 - 2.3. Thermal data from DSC and TGA investigations as well as molecular weight data are listed in these tables.

A TGA study of toluenesulfonic acid catalyzed decomposition of these PEPU copolymers revealed little acid catalysis. The initial decomposition temperature of a number of samples was significantly depressed, however the temperature at which the first 10% weight loss occurred was little affected. TGA data are summarized in Table 4. As a consequence acid sensitive soft segments are being synthesized (see below).

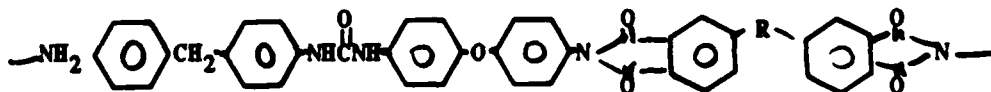
III. PEPI Copolymers

PEPI copolymers with hard blocks based upon MDI and pyromellitic dianhydride, e.g.,



have been prepared using PPO of $\bar{M}_n = 2000$ and 4000 and with incorporation of the bonding agent dihydroxyethylhydantoin. These are designated Series A and are listed in Tables 2.5 and 2.6.

A second series of PEPI copolymers is being studied. This series is prepared by capping PPO using the diisocyanate MDI and chain extension using 4,4'-diamino-diphenylether and various di-carboxylic anhydrides to build hard segments between the PPO units. The hard segment will have the composition shown below.



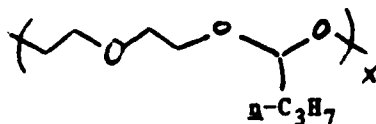
Initially polymers containing hard segment only have been synthesized while di-anhydride structure was varied to adjust the melting temperature of the hard segments. Results are shown in Table 2.7.

A series of PEPI copolymers using these dianhydrides is being synthesized and characterized. These materials will be too high melting for use as a LOVA binder. However, if the thermal properties of the copolymer hard blocks closely resemble those of the hard blocks alone we will have demonstrated phase independence in this thermal transition. Furthermore this simple strategy for rapid hard phase evaluation could be applied to other copolymer systems.

IV. Acid Sensitive Soft Segments

Both polyaldehydes and polyacetals are being studied. Polybutyraldehyde of $\bar{M}_n = 1000$ has been prepared and shown to be stable when capped. It is a

gummy rubbery material. Polyacetal has been prepared from diethylene glycol and butyraldehyde (see below) with $\bar{M}_n = 1800$.



Both of these polymers decompose in the 100 - 150° range with strong acid catalysis. They are currently being incorporated into PEPU type polymers.

3. LOVA POLYMER CHARACTERIZATION

I. Introduction

Propellant binders must serve many functions. They are a major component of a propellant fuel and act as the binding matrix which holds these highly filled composites together. Having good mechanical properties over a broad range of temperatures and rates of deformation is a requirement for most propellant systems, and this too is largely dependent on the matrix characteristics and its chemical and physical interactions with the particulate fillers contained within the matrix.

There have been many types of binders. For many years, the cast cure process based on chemically crosslinked thermosetting materials has been widely adopted. The process has its advantages, as the polymer is built up by reacting lower molecular weight prepolymers and additional chemical reactions can be included to promote or improve filler-binder interactions. Also, the low viscosity of the prepolymers facilitates the incorporation of high filler

content. However, there are several disadvantages in the use of crosslinked systems. Since reaction starts soon after mixing, the mass or grain has to be shaped before cure. The later stages of the reaction may become extremely slow or incomplete because of stoichiometric imbalance, presence of impurities like water in polyurethane systems, etc. Though widely used, crosslinked systems are less applicable to small masses or grains. In these cases, a thermoplastic binder is preferred, and the filler is incorporated in the melt. These systems, however, lead to excessively high viscosities after being filled, which makes processing very difficult.

An alternative to the previous processes is given by the use of thermoplastic elastomers. These systems are characterized by a structure based on physical rather than chemical crosslinks. These can be reversibly destroyed by heat in order to permit flow and processing. These materials are commercially available, but formulations are normally useful for molded objects substituting for conventional crosslinked rubbers. A first disadvantage is the high molecular weight, which results in poor processing characteristics after incorporation of the filler. A second disadvantage is the lack of flexibility in property formulation by chemical modifications.

On this basis, new thermoplastic elastomer systems have been developed especially as candidates for LOVA binders. Two main series of copolymers, polyether-polyurethane (PEPU) and polyether-polyimide (PEPI) have been synthesized with a variety of chain extenders and in different stoichiometric ratios (percentage of hard segments). A detailed description is presented in Table 3.1. According to the adopted nomenclature,

PEPU A(X-Y-Z)

PEPI A(X-Y-Z)

after the series name. A notes the type of chain extender, X are the moles of soft segments, Y are the moles of capping agent, and Z are the moles of chain extender.

The synthesis strategy for the PEPU series consists of the reaction of polypropylene oxide (PPO) with 1,4 diphenyl methane diisocyanate (MDI) as capping agent to form a capped diol. This further reacts with the chain extender.

The PEPI series have been prepared by reaction (in different ratios) of polypropylene oxide diol (PPO) with 1,4 diphenyl methane diisocyanate (MDI). The capped diol reacts with pyromellitic dianhydride to form a segmented polyether-polyimide copolymer. A detailed description of synthesis aspects can be found in specific reports.

A particular advantage in the use of thermoplastic elastomers as binders is the flexibility to modify composition ratios and chain extenders, which results in a wide spectrum of properties.

Although few quantitative relations exist between the mechanical properties of binders and those of filled systems, certain mechanical properties are desired in a binder. For example, the solid boundaries created by the filler will concentrate all the deformation in the matrix, which should be able to undergo large deformations to avoid failure. Therefore, a desirable feature in a binder is the capacity of an exceedingly large deformation at break, which can be associated with better impact resistance without brittle fracture. Also, a considerably low elastic modulus is required for a binder before reinforcement by the filler. Consequently, a simple tensile test yields useful information for preliminary conclusions on

the applicability of a certain copolymer structure and composition. The ideal binder should have adequate thermal transitions for mechanical performance and processing characteristics; should be chemically stable for long periods in contact with the oxidizer. Many other aspects have to be considered in weighing the relative merits of potential binders like oxygen balances, density, etc. It is improbable that a binder which fulfills all of these requirements can be found; however, in developing new propellants, all these factors should be considered.

Characterization of unfilled thermoplastic elastomers is a complex task given the multiphase character of these materials. The incorporation of the filler creates additional problems which originate in complex interactions at the new filler-binder interface.

In the present mechanics studies, a variety of experimental techniques are employed. In general, the same techniques are applied to both filled and unfilled polymers. A few methods, such as dilatation induced by straining, are specific to the composite materials.

Two types of experiments have been conducted: 1) screening experiments on new candidates, and 2) complete characterization of materials proven to be of interest in that their properties fall into the correct range and they are processable in the correct window of interest. A brief discussion on some experimental techniques is presented below.

II. Mechanical Testing - Experimental Techniques

1. Screening experiments

The following tests are routinely used as screening experiments:

Tensile tests: at a few select temperatures (-40°C , 25°C , and 50°C) to determine modulus, strength and strain at rupture. These experiments are conducted at slow strains, i.e. 2 cm/min.

Dynamical mechanical thermal analysis (DMTA): this type of analysis typical for study of multiphase polymers, is based on the harmonic distortion of a material sample (beam) with simultaneous temperature scanning. These experiments are conducted at frequencies of 1 Hz and temperatures between -100°C to 200°C . These experiments provide modulus and damping characteristics as well as information on thermal transitions (soft, hard segments).

2. Complete characterization

Several techniques are available to evaluate the mechanical properties of thermoplastic elastomers and their composites in the mechanics laboratory. Tests for such characterizations consist of the following:

Tensile and compression: these tests are conducted in a uniaxial mode over a broad range of temperatures (-75°C to $+80^{\circ}\text{C}$) and strain rates (0.001 min^{-1} to 3000 min^{-1}). These tests provide the basis for failure and response characterization.

DMTA: these tests are conducted in a bending mode to provide modulus and damping data as a function of temperature and frequency. Data on thermal transitions are also available from this experiment.

Creep: creep experiments are conducted at a variety of stress levels and temperatures to yield viscoelastic response data and creep to rupture failure data.

Stress relaxation: these experiments are conducted at several temperatures

and strain magnitudes to determine the viscoelastic response and time-temperature equivalence relations.

Strain dilatation: this type of strain-induced volume change is the best method to study dewetting and other cavitation phenomena. The specially designed dilatometers in the mechanics laboratory can function over a wide range of conditions including pressure, temperature and strain rate and are used to characterize composite candidates and study binder-filler interaction.

The experimental methods described above are used in several studies in order to develop several basic types of understanding for these polymers and their composites. The primary studies planned are described below:

Structure-property relations: the structure-properties relations between composites and their unfilled binders is not well understood. The addition of large amounts of particulate filler causes increased time dependence, cavitation and large increases in stiffness with corresponding decreases in elongation. There have been no systematic studies on highly filled-thermoplastic elastomers and few thorough studies on any filled polymers of interest to this program. Our group has had considerable experience in composite theory and experimentation and will attempt to develop theoretical and experimental relations describing the composite properties as a function of filler content and binder properties. Similar work will be performed in conjunction with the physical chemistry specialists to establish relations between chemical structure and binder properties. In the composite studies the filler levels are varied up to 60 volume percent calcium carbonate, potassium chloride and glass spheres.

3. Constitutive and failure characterization

The data provided by all these studies can be used to determine the

appropriateness of various constitutive response theories to the observed response including linear and non-linear viscoelastic theories. Stress-relaxation data and constant-strain rate data at different temperatures can be used to determine time-temperature equivalence relations. Tensile and creep failure data can be used to test various time and temperature dependent failure theories. Without meaningful constitutive and failure theories and data, it is almost impossible to perform any type of engineering analysis on materials.

4. Aging studies

The thermal and oxidative stability of the materials involved in the program are of great interest. Since these materials are being specifically designed to chemically degrade under certain conditions in an energy consuming manner, it is useful to know that no aging effects alter their behavior. For this reason, a few simple aging experiments are planned on selected candidates to check for properties variations in time due to chemical or physical mechanisms.

5. Binder-filler adhesion

The strain dilatation methods available in our laboratories provide an excellent method of studying binder-filler interactions as a function of chemical modification and processing techniques. These methods have already demonstrated success in the rocket propellant area. Their extension to gun propellants to evaluate the influence of chemical/filler surface modification and processing on dewetting, prove valuable in understanding the behavior of these materials. Although studies are conducted using inert fillers such as calcium carbonate, glass beads and KCl, conclusions are equally useful in marking trends in the development of real propellants.

III. Experimental Results

1. Unfilled materials

Tensile tests

Samples for tensile tests of unfilled materials were prepared by dissolving the polymers in DMF and then evaporating the solvent. DMF residues were eliminated by heating at 50°C under vacuum for 48 hours. Samples with thicknesses in the order of 1 mm to 1.5 mm were shaped according to ASTM standards (#5) and studied under tensile tests with crosshead speed of 2 cm/min. Results are presented in Figures 3.1, 3.2 and 3.3, and in Tables 3.2, 3.3 and 3.4.

The best properties (elongations in the order of 2000%) were obtained with PEPU Bi 121 and PEPU Bi 352. The first of these materials was selected for a more detailed study including interaction with different fillers.

Transitions and morphology

The transition temperatures of PEPU and PEPI unfilled materials were studied by DMTA (dynamical mechanical thermal analysis) by scanning temperatures between -70°C to 200°C. The results are in good agreement with estimations by other techniques like DSC (differential scanning calorimetry) and DMA (dynamic mechanical analysis). All materials present well defined soft segment transitions between -30°C and -15°C. At higher temperatures, the PEPU polymers exhibit a rather pronounced decay in modulus and become liquids above 80°C. At that temperature and above, it is possible to melt process the material without difficulty. The PEPI polymers, however, do not present sharp transitions, and cannot be melted below certain critical temperature for chemical decomposition. An exception is PEPI 121. This material can be

compression-molded at temperatures above 100°C, but in view of its extremely low elongation at break, further studies on this material were not encouraged at this point. Results from DMTA are presented in Figures 3.4 and 3.5, and in Table 3.6.

PEPU and PEPI materials were tested under cyclic loading in order to evaluate the percentage of hysteresis. This quantity provides some insight on the soft and hard segment domain morphology and is also useful for comparison of different copolymer compositions. As indicated in Figure 3.6a, the percentage of hysteresis is defined as the ratio between the area of the cycle (dissipated energy) and the total area under the loading curve (total energy input). The irreversible energy loss during cyclic loading in a tensile experiment can be used as a measure of the interconnectedness of the hard segment domains. The hysteresis results from the breaking of the interconnected hard segment domain through mechanical orientation. More interconnectedness is related to better ultimate properties. Results of this test for unfilled samples are presented in Figure 3.6b. Other experiments on tensile relaxation and permanent set of unfilled are included in Figures 3.7 and 3.8.

2. Filled materials

As a conclusion from screening tests, PEPU Bi 121 presented adequate characteristics as binder and its mechanical behavior was studied with different fillers KCl, CaCO_3 and glass beads with loads up to 70 volume percent.

Transitions and morphology

Transitions in filled PEPU at different glass bead content were

studied by DMTA in experiments similar to those for unfilled systems (Figures 3.9 and 3.10). Analogous trends are observed. In the presence of filler, hysteresis is increased by 15% in comparison with unfilled samples (Figure 3.11). Tensile relaxation and permanent set experiments are presented in Figures 3.12 and 3.13. For strains below 20% the permanent set is nearly independent of the filler content.

Tensile and compression tests

PEPU Bi 121 was filled with CaCO_3 at levels of 40, 50 and 60 volume percent by addition of solvent and subsequent evaporation. All these materials were easily melted at 100°C and extruded in a ram extruder to obtain cylindrical strands of about 4.5 mm diameter. These strands representing excellent models for the final geometry of propellants, were tested under tension, tension relaxation, compression and compression relaxation. The strands were cut into rods 25 mm long and 10 mm long, and their ends were glued to flat plates between grips. Longer samples were tested in tension and tension relaxation (Figures 3.15 and 3.16 and Table 3.7). Shorter samples were tested in compression and compression relaxation (Figures 3.16 and 3.17 and Table 3.7). All these tests indicate a satisfactory mechanical response as binder.

Stress-strain-dilatation studies

Mechanical behavior of particulate filled polymers is influenced by separation of filler particles from the matrix. Vacuoles form and start to grow when the particles dewet from the polymer during deformation. The process of vacuole formation and growth lead to lower reinforcement by the filler; the material finally becomes unstable and fails. A measure of the

loss of reinforcement caused by separation of the filler from the matrix can be obtained by monitoring the volume change of the composite. Combined mechanical-dilatational studies can provide a means of distinguishing the non-linear effects due to cavitation from other nonlinearities encountered in this type of materials. Farris' dilatometer permits study of binder-filler interactions as a function of chemical modification and processing conditions.

Preliminary stress-strain-dilatation tests were performed on PEPU Bi 121 filled with glass beads to 40 volume percent. Cylindrical specimen of 1 cm in diameter by 8 cm long were prepared by melting the filled material in the barrel of an Instron Capillary Rheometer at 80°C, 90°C and 100°C. Stress-strain-dilatation curves ($\dot{\epsilon} = 4$ cm/min) show nearly identical behavior for the three samples, as indicated in Figures 3.18, 3.19 and 3.20. For the case of glass spheres, filler-binder separation starts at rather low strains, what suggests the need to improve adhesion, possibly through chemical agents. Similar tests on other fillers and on wide ranges of temperature are being developed.

Conclusions and significance

During this period, a large number of thermoplastic elastomers as LCVA binders have been tested for mechanical performance. Elementary tests have been used to screen materials of interest, which were then subjected to a more complete investigation after incorporation of fillers. Until now, there have been few systematic studies of particulate filled composites using extensive experimental methods as developed in this program, and probably no one related to thermoplastic elastomers as binders. The present studies on mechanical properties, in coordination with investigations in processing and

synthesis, have produced a considerable amount of information. This experience is most valuable for understanding structure-property relations and for orienting further synthesis efforts.

4. LOVA POLYMER RHEOLOGY AND PROCESSING

The research has the objective to develop fundamental knowledge which, in the future, will help to process LOVA propellants. The main emphasis is given to non-Newtonian rheology: measurement of rheological properties, development of new techniques for rheological characterization, and formulation of rheological constitutive equations. A second emphasis is given to the application of the measured rheological data to the study of stress fields in complex flows of polymer processing. This requires the development of new tracking techniques with which we can follow individual material elements in the flow.

I. Development of Rheometrical Techniques

The development of a constitutive equation requires experimental information on the flow behavior. This information can partially be gained by conventional methods (oscillatory shear in rotational rheometer, steady shear in capillary rheometer). However, new techniques have to be found to measure the transient stress in a material with changing structure (like the LOVA systems). The following describes such new experimental techniques for measuring the large strain behavior in shear and extension, the start-up in equibiaxial extension, and the slip velocity of the fluid on the wall. These techniques have been developed during the first part of this contract.

Large Step Strain Experiments

The parallel plate rotational rheometer is a standard instrument for measuring the small strain behavior of polymeric materials. However, data from large strain experiments could not be interpreted since the strain in the sample is inhomogeneous. Within this contract, we developed and tested a method which overcomes this handicap. The results are given in a separate report which is accepted for publication in the Journal of Rheology.

Monitoring Material Changes with Oscillatory Shear

The stress response of a linear viscoelastic liquid to sinusoidally oscillating shear is a sine function in time, with the same frequency as the strain, but with a phase shift, δ . For a given strain

$$\gamma = \gamma_0 \sin(\omega t)$$

the stress response will be

$$\begin{aligned} \tau &= G^* \gamma_0 \sin(\omega t + \delta) \\ &= G^* \gamma_0 \cos \delta \sin \omega t + G^* \sin \delta \cos \omega t \end{aligned}$$

where $G' = G^* \cos \delta$ = dynamic storage modulus

$G'' = G^* \sin \delta$ = dynamic loss modulus

$$\tan \delta = \frac{G''}{G'} = \text{loss tangent}$$

The dynamic storage modulus is a measure of the elasticity of a material, and the dynamic loss modulus is a measure of the viscosity of a material.

Oscillatory shear experiments were performed using a Rheometrics Dynamic Spectrometer, which can be equipped with a cone and plate or with parallel plates (see Figure 4.1). In the cone and plate geometry is sheared the sample homogeneously, which allows measurement of the primary normal stress difference and of shear strain-dependent properties. For filled systems, if

the size of the filler particles are comparable to the clearance between the cone and the plate, the cone and plate cannot be used.

Parallel plate geometry creates an inhomogeneous shear flow, but sample preparation is easier than for the cone and plate experiment. Highly filled liquids can slip at solid surfaces and plates with radial serrations must be used for large shear experiments to prevent slipping. Serrated plates were used to measure the dynamic moduli of cellulose acetate butyrate filled to 55 vol% with calcium carbonate (Georgia Marble Gamasperse 6532), Figure 4.2.

Measurement of Slip Velocity

The slipping phenomenon can be examined in flow through capillaries, Figures 4.3 and 4.4. The slip velocity at the wall of the capillary can be calculated from measurements made with capillaries of different radii. For a material flowing through a capillary, the shear stress is given by

$$\tau = \frac{r}{2} \frac{\Delta P}{L}$$

where ΔP is the pressure drop across the capillary

L is the length of the capillary

r is radial distance (from the axis of the capillary)

At the capillary wall, the shear stress is

$$\tau_R = \frac{R \Delta P}{2L}$$

The volumetric flow rate through a capillary is given by

$$Q = \pi R^3 \left(\frac{V_s}{R} + \frac{1}{\tau_w} \int_0^{\tau_w} \tau^2 d\tau \right)$$

or,

$$\frac{Q}{\pi R^3} = \frac{V_s}{R} + f(\tau_w)$$

where

V_s = velocity at the capillary wall, or, the slip velocity.

$f(\tau_w)$ = a function only of τ_w

Here, the assumption has been made that the slip velocity for a given material is a function only of τ_w .

These equations are utilized in a new method for measuring the slip velocity. The new method utilizes a twin-capillary: If the volumetric flow rates are measured for simultaneous extrusion through two capillaries, see Figure 4.5, in which the shear stress at the wall, τ_w , is the same, the slip velocity may be calculated as

$$V_s = \frac{\frac{Q_1}{\pi R_1^3} - \frac{Q_2}{\pi R_2^3}}{\frac{1}{R_1} - \frac{1}{R_2}}$$

The condition of having the same wall shear stress, τ_w , in both capillaries is achieved by imposing the same pressure drop across two capillaries with the same length-to-radius ratio. A die is being constructed with two capillaries of radii 0.5 mm and 1.0 mm, both having a length-to-radius ratio of 30. By measuring the pressure drop at various flow rates, it is possible to obtain the slip velocity as a function of shear stress. The volumetric flow rate, Q , through each capillary is written as a sum of the contribution of slipping and the contribution of deformation,

$$Q = \pi R^2 V_s + Q_d$$

The shear rate at the wall, $\dot{\gamma}_w$, is given in terms of the flow rate due to deformation and the shear stress at the wall:

$$\dot{\gamma}_w = \frac{1}{\pi R^3} (3Q_d + \tau_w \frac{dQ_d}{d\tau_w})$$

II. Rheological Characterization

A Rheometrics Dynamical Spectrometer was used to measure the linear viscoelastic properties of LOVA candidates in oscillatory shear. The temperature dependence of the dynamic moduli of a series of polyether-polyurethane systems reveal that changes in the mole ratio of polyether to polyurethane change the dynamic moduli of the solid copolymer, but do not change the melting point. Altering the molecular structure of the polyurethane segment changes the melting point of the copolymer, see Figure 4.6.

Filled homopolymers were investigated as model systems. Figure 4.7 shows the shear stress of a polyether triol (BASF TP-2540) filled to 50 vol% with calcium carbonate (Georgia Marble Gamasperse 6532, 2 - 10 μ) as measured by capillary rheometry. The data were separated to yield the steady shear viscosity, Figure 4.8, and the slip velocity, Figure 4.9. Polydimethylsiloxane (General Electric SE30) filled to 50 vol% with calcium carbonate (Georgia Marble Gamasperse 6532) was subjected to oscillatory shear in a cone and plate rheometer, and the stress response appeared to depend on the shear history in an unexpected way. The shear program and the dynamic moduli are shown in Figure 4.10.

The viscosity of the CaCO_3 -filled polydimethyl siloxane in equibiaxial extension was measured by lubricated squeezing. The viscosity curves do not superimpose, which indicates non-linear behavior (see Figure 4.11). The experimental results will be modelled by a rheological constitutive equation. Several approaches are under investigation.

III. Fundamentals of LOVA Processing

The processing studies concentrated on two areas: a feasibility study

of LOVA processing and development of modelling techniques for polymer processing. These modelling techniques will be the basis die design for the extrusion of gun propellants.

Feasibility Studies

One of the LOVA binders, PEPI (Bi 1-2-1), as polymerized at the University of Massachusetts was filled with Calcium Carbonate, 40%, 50%, and 60% by volume. The filled system was extruded with a ram extruder on which we mounted a seven-pin small grain size LOVA extrusion die (supplied by Indian Head), Figure 4.12. Measured extrusion pressures are given in Figure 4.13. The perforations of the extrudate were regular, and the surface was smooth. Mechanical properties of the extrudates were measured by Professor Farris. TEM micrographs were obtained by Dr. J. Roccio.

Since there were no processing results available on the use of a co-rotating twin screw extruder, we decided to perform test runs and demonstrate the feasibility of the process. Tests were made with a twin screw extruder at Werner and Pfleiderer Corp. in Ramsey, New Jersey. The machine used was a fully intermeshing co-rotating twin screw extruder with 2-flite screws. The screws were 28 mm in diameter and 110 cm in length. A single strand was extruded through a 7-perforation gun propellant die, 0.186 inches in diameter. Solid ingredients were fed as powders by gravimetric feeders. Liquids were fed by positive displacement pumps which were calibrated to deliver known mass flow rates. Temperature control was provided in four zones of the extruder barrel and for the die. The pressure just upstream of the die was measured and the power consumption of the extruder were measured. Three formulations were tried:

1. DuPont Hytrel thermoplastic elastomer as a binder

Calcium carbonate as a simulant for RDX

Trichloroethylene as a solvent

2. CAB (cellulose acetate butyrate) as a binder

Powdered sugar as a simulant

Citrate plasticizer

Ethylacetate and ethanol as solvents

3. CAB as a binder

Calcium carbonate as a simulant

Citrate as plasticizer

Ethylacetate and ethanol as solvents

DuPont Hytrel is a polyether-polyester copolymer. It was chosen for these tests since its physical properties are similar to copolymers developed at UMass for LOVA binders.

For the first formulation, the extruder was set up as shown in Figure 4.14. Extrusion pressures were relatively large. The high temperatures were necessitated by the high melting point of the Hytrel (140 - 160°C). The solvent was seen to evaporate out of the port through which the calcium carbonate was fed and probably did not aid the processibility of the filled binder downstream. The strand was extruded at 16 ft/min., and was smooth.

For the second formulation, the second solids feed port was closed and the solids were fed together (Figure 4.15). The extrusion pressure was approximately 700 psi and the power consumption was 1.2 kW. The strand was extruded at 3.5 ft/min., and was smooth, but quite soft, still containing about 10% by wt. solvent. The cross section is shown in Figure 4.17.

For the third formulation, the same set up was tried. The extrusion pressure was 800 psi and the power consumption was 1.45 kW. This formulation contained much less solvent and gave a smooth extrudate.

The extruder provided very good mixing and extrudates were homogeneous. Pressures attainable with this machine were large enough to extrude at high rates, even at the low RPM used in these tests.

Modelling of Stress Fields in Complex Die Flows

The prediction of the processing behavior of polymeric materials (such as the filled LOVA system) is not possible with state of the art methods. Further research is required to further the understanding of the stress development in complex flows. For this purpose, we have derived a tracking method for material elements in steady axisymmetric flows (H.H. Winter, J. Non-Newtonian Fluid Mech. 10, 157-167 (1982)). With this method, we can follow individual material elements in processing flows and calculate the developing stress as described by a memory integral constitutive equation. As the next step, we set out to test our tracking method with flow through an annular extrusion die. The die of Figure 4.17 has been completed recently. The end section of the die is made out of glass. For stress measurements, polarized laser light is shined radially through this transparent die section and the polymer within the die. The measured stress will be compared with the calculated values from the tracking model.

TABLE 2.1. PHYSICAL PROPERTIES OF POLY(PROPYLENE-OXIDE-URETHANE)
BLOCK COPOLYMERS FROM MDI

Sample	Cat.	Mn	Mw	MWD	$[\eta] =$ dl/g	T ₁	T ₂	T ₃	DC	Wt.% of hard bl
B,1-2-1	--	13158	22817	1.73	0.12	-36	70	140	5.0	22.6
B,1-2-1	Et ₃ N	21377	51514	2.41	0.29	-36	70	138	8.2	22.6
B,1-2-1	Tin	55796	85157	1.53	0.52	-36	70	138	21.6	22.6
B,1-3-2	Et ₃ N	33517	126628	3.78	0.34	-36	72	194	11.4	31.9
B,1-3-2	Tin	70182	120608	1.72	0.52	-36	72	194	24.3	31.8
Bn,1-2-1	Tin	31969	61554	1.93	0.37	---	99.5	---	11.8	25.9
Bt,1-3-2	Tin	30733	67512	2.20	0.43	-51	138	---	9.45	38.9
Bt,2-5-3	Tin	31052	65520	2.11	0.39	-51	134	---	10.35	33.4
Bt,1-2-1	Tin	30915	69898	2.26	0.36	-52	133.4	---	11.24	27.3
Bt,3-5-2	Tin	30497	65569	2.15	0.35	-51	133	---	11.80	22.7
Bi,1-3-2	Tin	31004	60457	1.95	0.24	-23	127.5	168.5	9.5	38.9
Bi,2-5-3	Tin	31135	57077	1.83	0.24	-35	127.5	168.5	10.4	33.4
Bi,1-2-1	Tin	43799	75473	1.72	0.65	-48	132	164	16.0	27.3
Bi,3-5-2	Tin	30843	57069	1.85	0.24	-50	127.5	161.2	11.9	22.7
Bi,2-3-1	Tin	30641	54234	1.77	0.22	-52	127.7	155.0	12.26	20.0

^aT₁, T₂ and T₃ were obtained from DSC.

^bDC = degree of condensation.

^cIntrinsic viscosity were measured in DMF at 25°C.

^dB_n, B_i and B_t were prepared from DMF solvent.

^eAverage molecular weight were obtained from GPC.

^fWeight percentage were obtained from calculation.

TABLE 2.2. SEGMENTED POLYETHER-POLYURETHANES (PEPU) COPOLYMERS
FROM TOLUENE DIISOCYANATE

Polymer ^a	Weight % Hard Block	[η]dL/g ^b	M_w^c	M_n^c	M_w/M_n^c	DSC (°C)			TGA (°C)	
						T_1	T_2	T_3	T_d	T_m
Bt(132)	33.91	0.18	32,206	16,006	2.01	-43	62	153	160	367.5
Bt(253)	28.94	0.20	44,832	20,337	2.2	-39	60	160	160	373.5
Bt(121)	23.1	0.26	62,792	27,512	2.3	-39	60	157	160	377.5
Bi(132)	33.91	0.15	30,975	16,041	1.93	-42	58	159	162.5	347
Bi(253)	28.94	0.17	40,647	19,194	2.11	-42	58	154	160	355
Bi(121)	23.1	0.17	41,260	19,655	2.1	-41.5	58	166	160	372

a. Bt = N,N'-bishydroxyethylterphthalamide, Bi = N,N'-bishydroxyethylisophthalamide.

b. Intrinsic viscosity in DMF at 25°C.

c. By gel permeation in THF, polystyrene standard.

d. T_d = initial decomposition temp. T_m = temp. of maximum decomposition rate.

TABLE 2.3. SEGMENTED POLYETHER-POLYURETHANE (PEPU) COPOLYMERS
FROM HEXAMETHYLENE DIISOCYANATE

Polymer ^a	Weight % Hard Block	$[\eta]$ dL/g ^b	M_w^c	T_1	OSC (°C) T_2	T_3	T_d	TGA (°C) ^d T_m
Bt(132)	33.5	---	56,500	-58	98	---	182.5	342.5
Bt(253)	28.5	---	56,500	-56.7	100	---	182	377
Bt(121)	22.8	0.39	55,000	-57	102.5	146	182	372.5
Bi(132)	33.5	0.21	52,000	-57.5	90	147	182	368
Bi(253)	28.5	0.165	52,000	-55	86	144	182	376
Bi(121)	22.8	0.315	72,000	-55	83	143	182	360

a. Bt = N,N'-bishydroxyethylterphthalamide, Bi = N,N'-bishydroxyethylisophthalamide.

b. Intrinsic viscosity in DMF at 25°C.

c. Gel permeation in N-methylpyrrolidone, polystyrene standard.

d. T_d = initial decomposition temp. T_m = temp. of maximum decomposition rate.

TABLE 2.4. TGA STUDY OF PEPU COPOLYMERS

Polymer	T _d	T _d *	T ₁₀	T ₁₀ *	T ₅₀	T ₅₀ *	Wt. %
MDI							
B-132	250	151	320	270	387	375	31.9
B-121	275	220	350	340	395	395	22.6
Bn-121	237	182	313	271	365	355	25.9
Bt-132	200	87.5	287.5	220	383	385	38.9
Bt-253	200	---	290	---	345	---	33.4
Bt-121	200	115	290	317	390	390	26.3
Bt-352	200	135	307	320	376	394	22.7
Bi-132	200	135	290	307.5	387	390	38.9
Bi-253	200	---	276	---	371	---	33.4
Bi-121	224	200	290	290	384	386	26.3
Bi-352	200	135	314	315	386	393	22.7
TDI							
Bt-132	160	108	260	282	362	382	33.9
Bt-253	160	108	265	295	372	392	28.9
Bt-121	160	108	275	310	378	375	23.1
Bi-132	160	107	265	265	347	327	33.9
Bi-253	160	107	257	287	355	381	28.9
Bi-121	160	107	265	287	372	381	23.1
HDI							
Bt-132	182.5	---	272.5	---	344	---	33.5
Bt-253	182	---	295	---	377	---	28.5
Bt-121	182.5	---	300	---	372	---	22.8
Bt-132	182.5	---	294	---	368	---	33.5
Bi-253	182.5	---	305	---	376	---	28.5
Bi-121	182.5	---	292.5	---	360	---	22.5

*Data obtained in the presence of p-toluene sulfonic acid, 1% by weight.

Table 2.5. PROPERTIES OF PEPI COPOLYMERS - SERIES A

	% Soft (by wt.)	$[\eta]^b$	Td ^c	Mn ^d	Mw ^d	Mw/Mn ^d	Tg (°C) ^e
PEPI-1320 ^a -II-12	62.77	0.320	250°C	—	—	—	177.5
PEPI-2530-II-32	67.75	---	225°C	—	—	—	156.5
PEPI-1210-II-21	73.58	0.31	200°C	44,647	77,324	1.73	155
PEPI-3520-II-41	78.06	0.295	250°C	30,307	47,911	1.58	—
PEPI-2310-II-32	80.52	0.275	225°C	33,845	65,280	1.93	129

^aThe numbers are ratio of reactants. ex. PEP-1320 = 1 mole PPO, 3 mole MDI, 2 Mole PMDA, 0% by volume filler.

^bIntrinsic viscosity was measured in DMF at 25°C.

^cTd (initial decomposition temp.) was obtained from TGA.

^dMolecular weight was obtained from Waters Associates GPC.

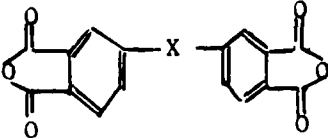
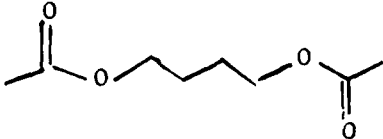
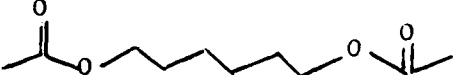
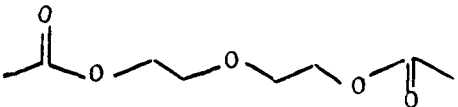
^eTg was obtained from DSC.

TABLE 2.6. SEGMENTED POLYETHER-POLYIMIDES (PEPI) - SERIES A

Polymer	Weight % Hard Block	$[\eta]$ dl/g ^c	M_w^f	M_n^f	M_w/M_n	DSC (°C)	
						T _g	T _d
132(H) ^a	37	0.22 ^d	---	--	---	-38	---
253(H)	32	--	---	--	---	-46	250
121(H)	26.5	0.285	54,000	8,400	6.4	-44	265
352(H)	22	0.41	220,000	39,000	5.7	-45	300
231(H)	19.5	0.55	150,000	30,000	4.8	-38	255
132(4K) ^b	23	0.382	103,000	28,000	3.8	-59	340
253(4K)	19	0.374 ^e	180,000	20,000	9.1	-58	350
121(4K)	15	0.156	---	--	---	-57	275
352(4K)	12	0.197	64,000	32,000	2.0	-59	250

^a5% of PPO replaced by di(hydroxyethyl)hydantoin.^bPPO, $M_n = 4,000$.^cIn DMF at 25°C.^dIn NMP at 25°C.^e0.177 in NMP.^fIn DMF.

TABLE 2.7. PEPI(B) HARD BLOCK ONLY
THERMAL PROPERTIES VS. CHEMICAL STRUCTURE

X in Dianhydride 	T ¹ (°K)	
	20°C/min	40°C/min
	557	560
	411	415
	407	409
	423	429

T¹ - DSC transition.

TABLE 2.8. CHARACTERISTICS OF PEPI(B)-121 POLYMERS

Chain Extender	PEPA	PEPI
BP	Tough	Toughest
BD	Less Tough More Elastic	Less Tough Cloudy Film
ED	Less Tough More Elastic	Less Tough Cloudy Film
DG	Less Tough More Elastic	Most Elastic Clear Film

TABLE 3.1. **LOVA MATERIALS**

SAMPLE PEP POLYETHER POLYURETHANE	CHAIN EXTENDER	WEIGHT % HARD BLOCK
B-132	1,4 BUTANE DIOL	31.9
B-121	"	22.6
BU-121	BIS (2-HYDROXYETHYL) HYDROQUINONE	25.9
BT-132	BIS (2-HYDROXYETHYL) TEREPHTALAMIDE	38.9
BT-253	"	33.4
BT-121	"	26.3
BT-352	"	22.7
BI-132	BIS (2-HYDROXYETHYL) ISOPHTALAMIDE	38.9
BI-253	"	33.4
BI-121	"	26.3
BI-352	"	22.7
BI-231	"	20.0
SAMPLE PEPI POLYETHER POLYIMIDE	CHAIN EXTENDER	
PEPI-132	PYROMELLITIC DIANHYDRIDE	37.0
PEPI-253	"	32.0
PEPI-121	"	26.0
PEPI-231	"	19.0
PEPA-253	4 AMINOPHENYL ETHER	34.0
PEPI-253	"	34.0

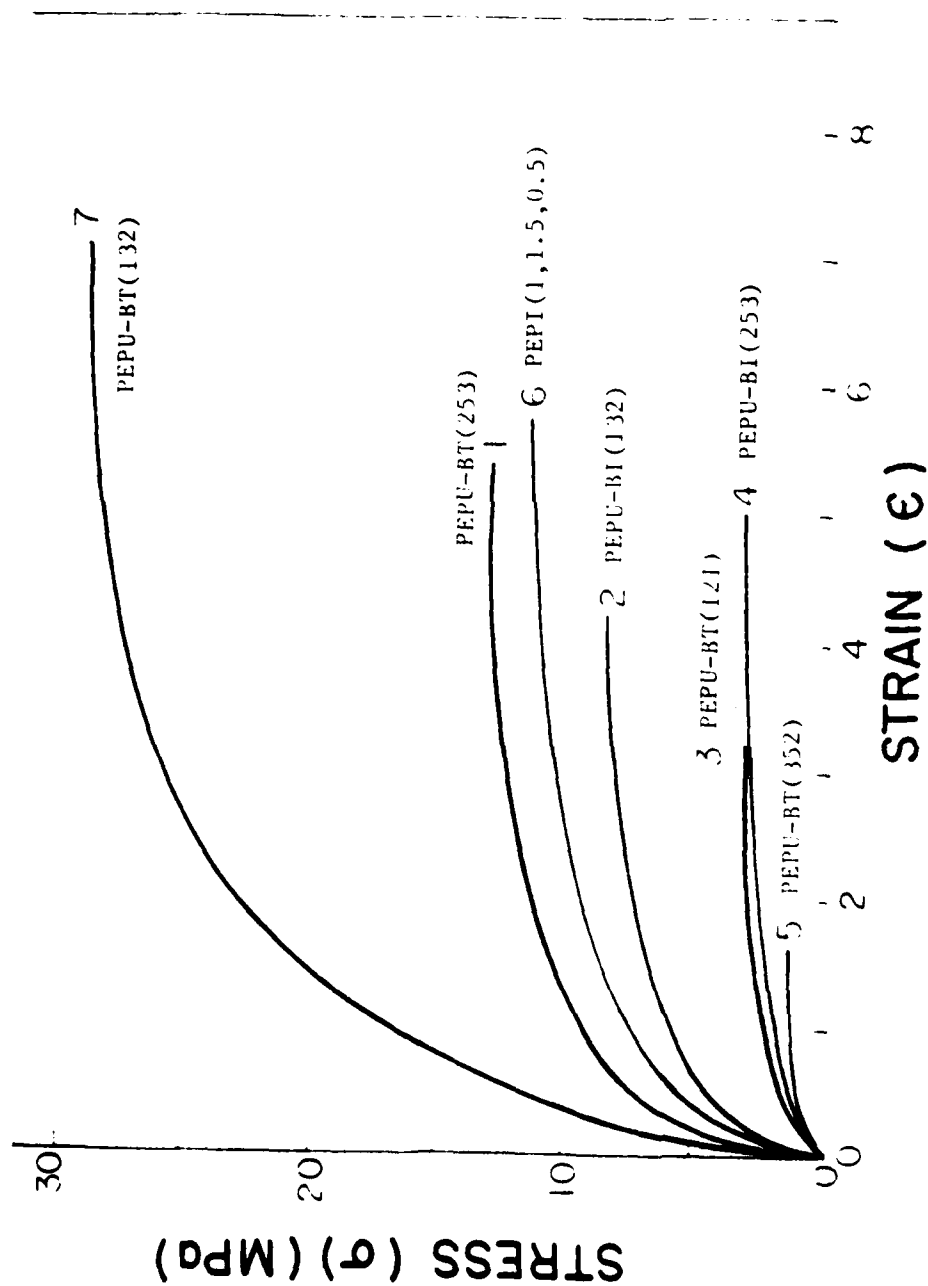


FIGURE 3.1 TENSILE TEST, STRESS-STRAIN RELATION
(UNFILLED SAMPLES)

TABLE 3.2. STRESS-STRAIN - TENSILE TEST UNFILLED MATERIALS

MATERIAL	E (MPa)	σ_B (MPa)	Z ELONG.
PEPU Bt(2-5-3)	29.0	12.8	530
PEPU B1(1-3-2)	7.6	8.6	420
PEPU Bt(1-2-1)	5.7	2.9	324
PEPU B1(2-5-3)	2.6	3.3	501
PEPU Bt(3-5-2)	8.2	1.6	149
PEPI (1-1.5-0.5)II32	7.7	11.5	574
PEPU Bt(1-3-2)	43.4	29.0	714

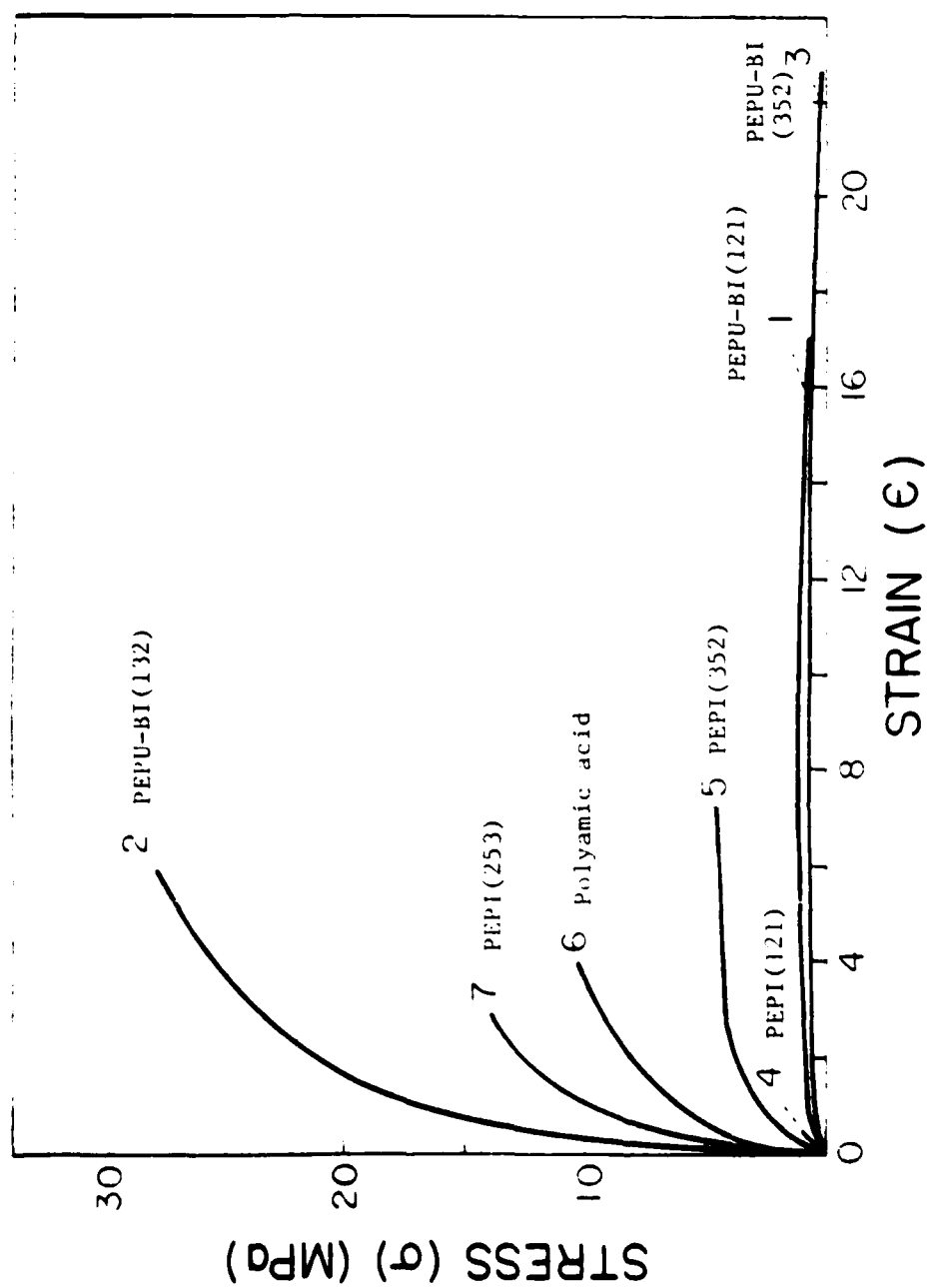


FIGURE 3.2 TENSILE TEST, STRESS-STRAIN RELATION - UN-FILLED MATERIALS

TABLE 3.3. STRESS-STRAIN (UNFILLED MATERIALS)

	Unfilled Samples	Tensile Test	
Sample	E [MPa]	σ_B [MPa]	% Elong.
PEPU-Bi-(121)	1.46	0.741	1,720
PEPU-Bi-(132)	17.38	27.0	673
PEPU-Bi-(352)	1.7	0.082	2,400
PEPI-(121)	2.0	1.27	60
PEPI-(352)	3.81	4.22	726
Polyamic Acid	9.71	10.64	400
PEPI(253) TRS	18.0	14.1	298

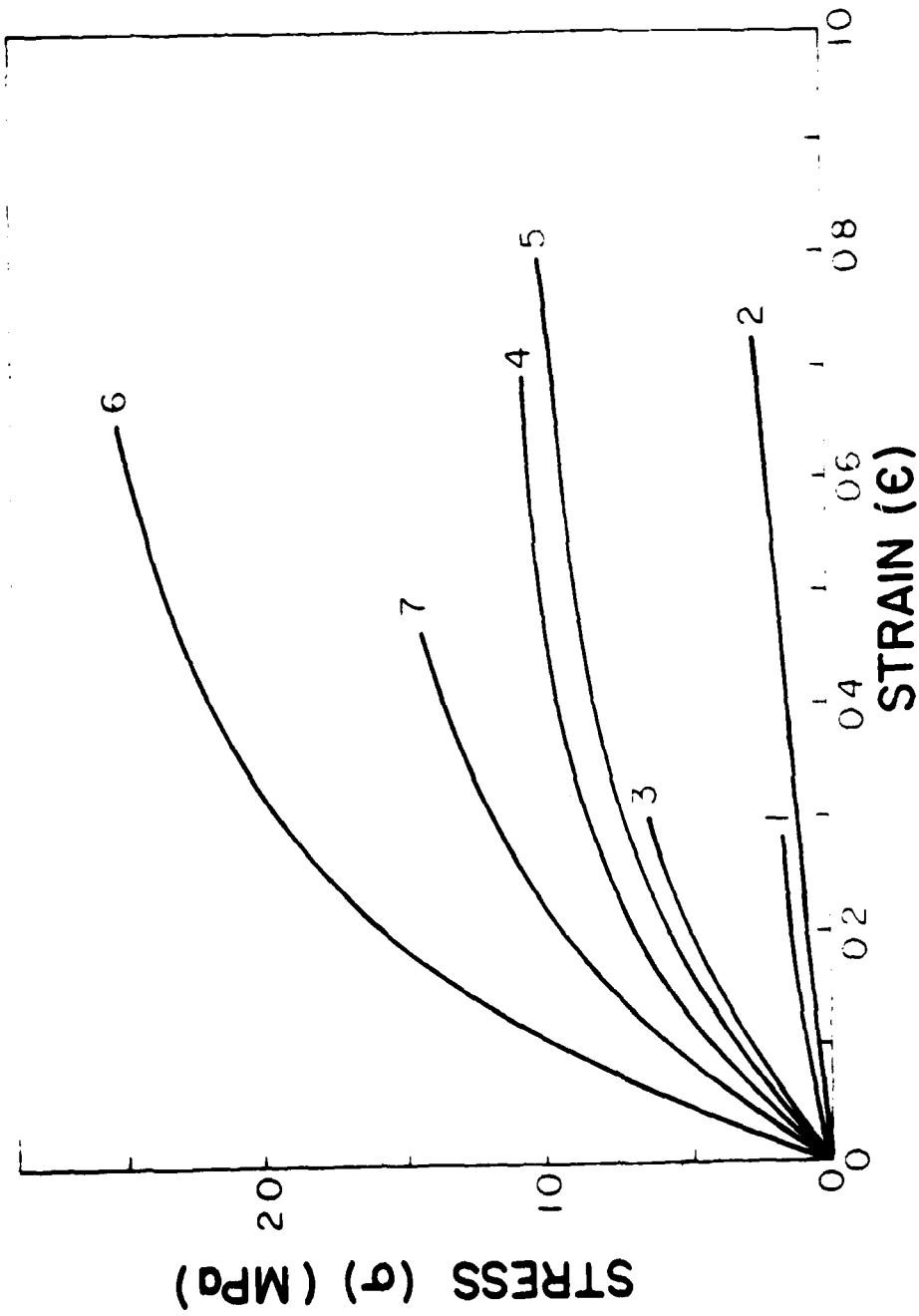


FIGURE 3.3 TENSILE TEST, STRESS-STRAIN RELATION
(UNFILLED SAMPLES)

TABLE 3.4. STRESS-STRAIN RELATION (UNFILLED SAMPLES)

Sample	E [MPa]	σ_B [MPa]	ϵ_B
PEPI 3512 (4000) II-61	0.97	0.16	0.28
PEPI 2310 (4000) II-99 S.C.	0.64	0.23	0.73
PEPI 1210 (H) II-67	2.67	0.60	0.3
PEPU 253 d(22) C.M.	3.9	1.05	0.69
PEPU 253 P(20) C.M.	3.3	1.01	0.8
PEPU 132 d(21) C.M.	8.11	2.5	0.66
PEPU 132 P(19) C.M.	5.5	1.41	0.46
PEPI 1210 (4000) II-60 C.M.	---	----	----

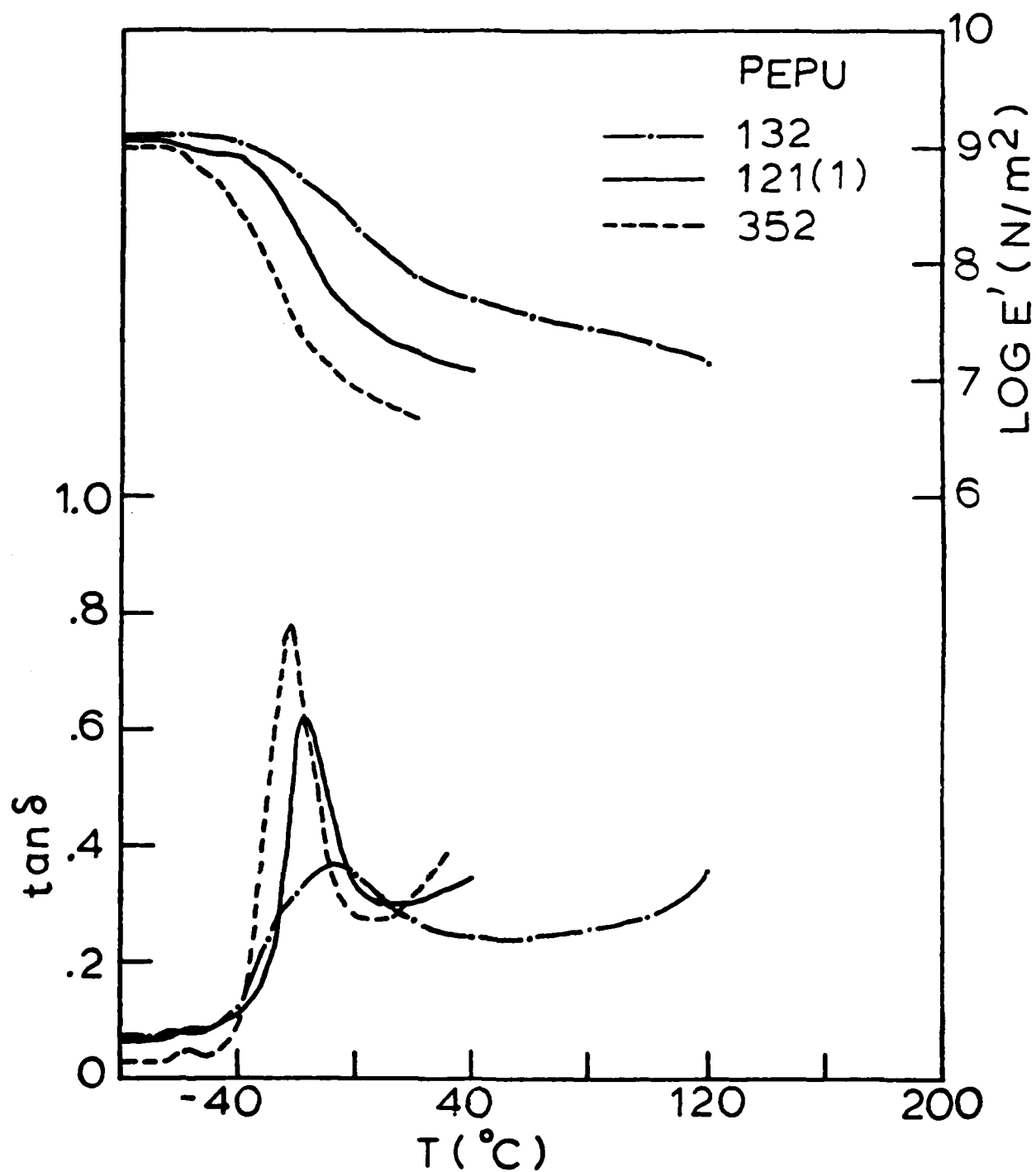


FIGURE 3.4 DMTA ANALYSIS FOR PEPU (UNFILLED)

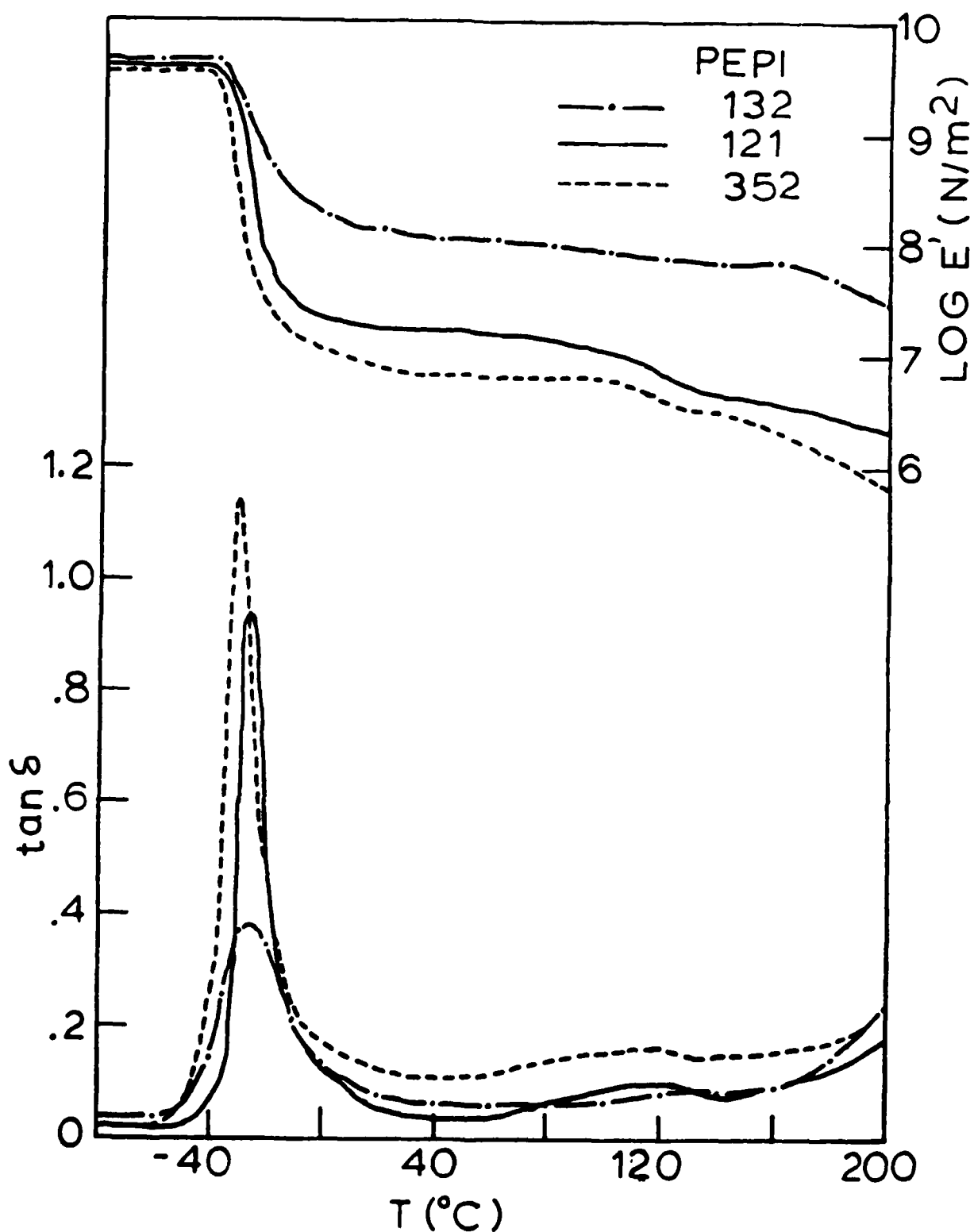


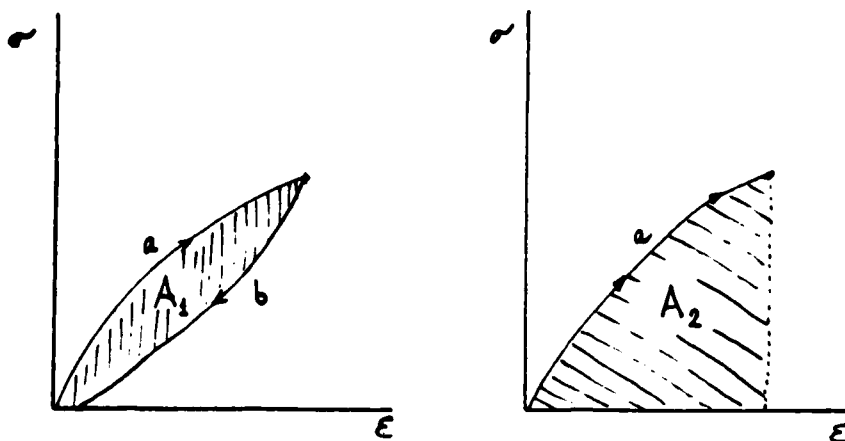
FIGURE 3.5. DMTA ANALYSIS FOR PEPI (UNFILLED)

TABLE 3.6. SUMMARY OF TRANSITION TEMPERATURES FROM DMTA*

DMTA 1°C/sec - 5°C/min

Sample	T _S (C)	T _H (C)
PEPI 352	-31	+115
PEPI 121	-27	+115
PEPI 253 TRS	-31	+117
PEPA 253 TRS	-25	+124
PEPU-BI-352	-48	--
PEPU-BI-121	-15	--
PEPU-BI-132	-25	--

*Programmed at 1° sec⁻¹ to 5° min⁻¹.



path a: loading
path b: unloading

$$\% \text{ HYSTERESIS} = (A_1 / A_2) \times 100$$

(All hysteresis experiments were performed at strain rates 10 mm/min)

FIGURE 3.6a. HYSTERESIS EXPERIMENTS.

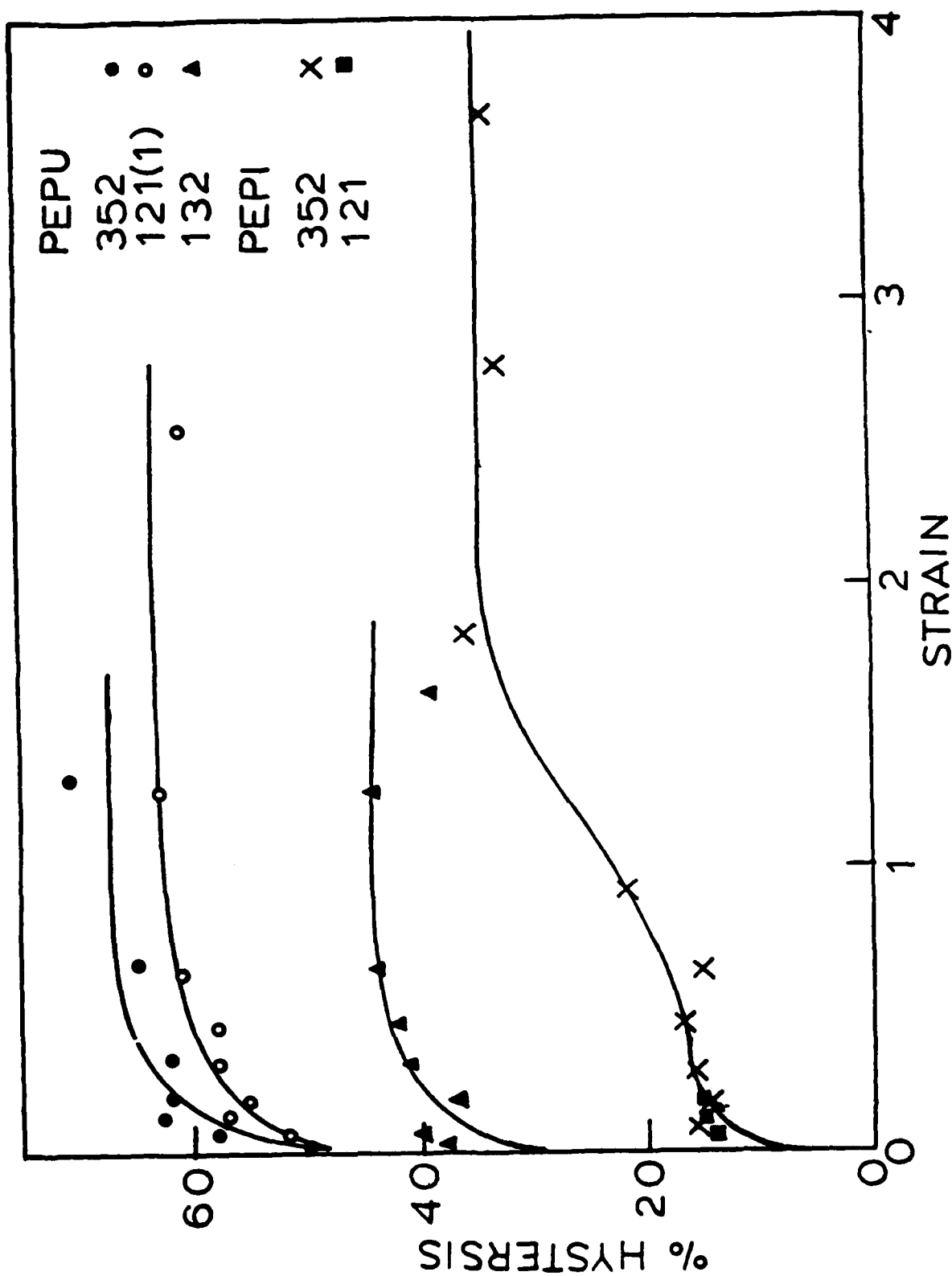


FIGURE 3.6b. HYSTERESIS VS. STRAIN (UNFILLED MATERIALS)

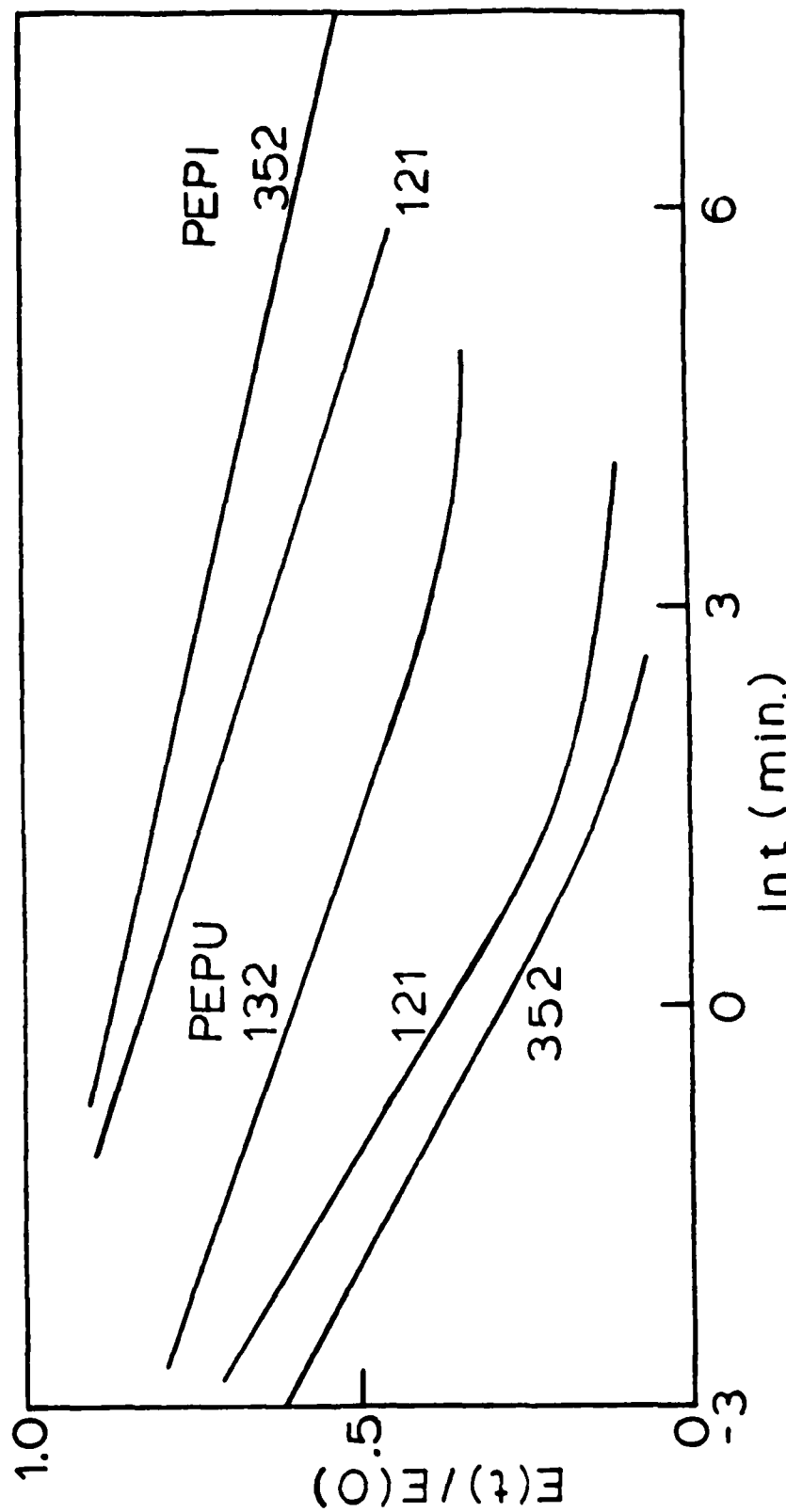


FIGURE 3.7. TENSILE RELAXATION EXPERIMENTS. RELATIVE MODULUS VS. TIME (UNFILLED MATERIALS)

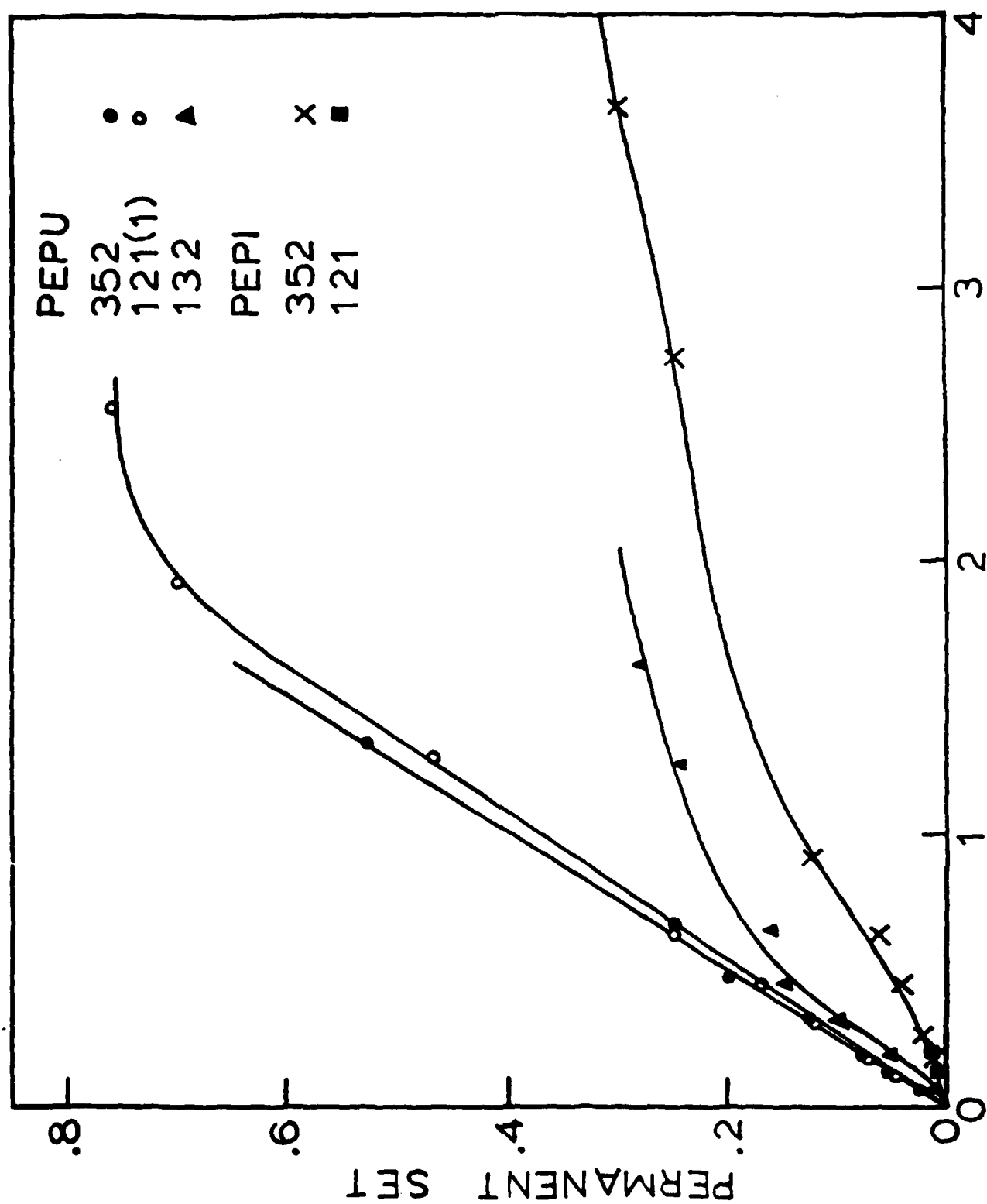


FIGURE 3.8. PERMANENT SET VS. STRAIN (UNFILLED MATERIALS)

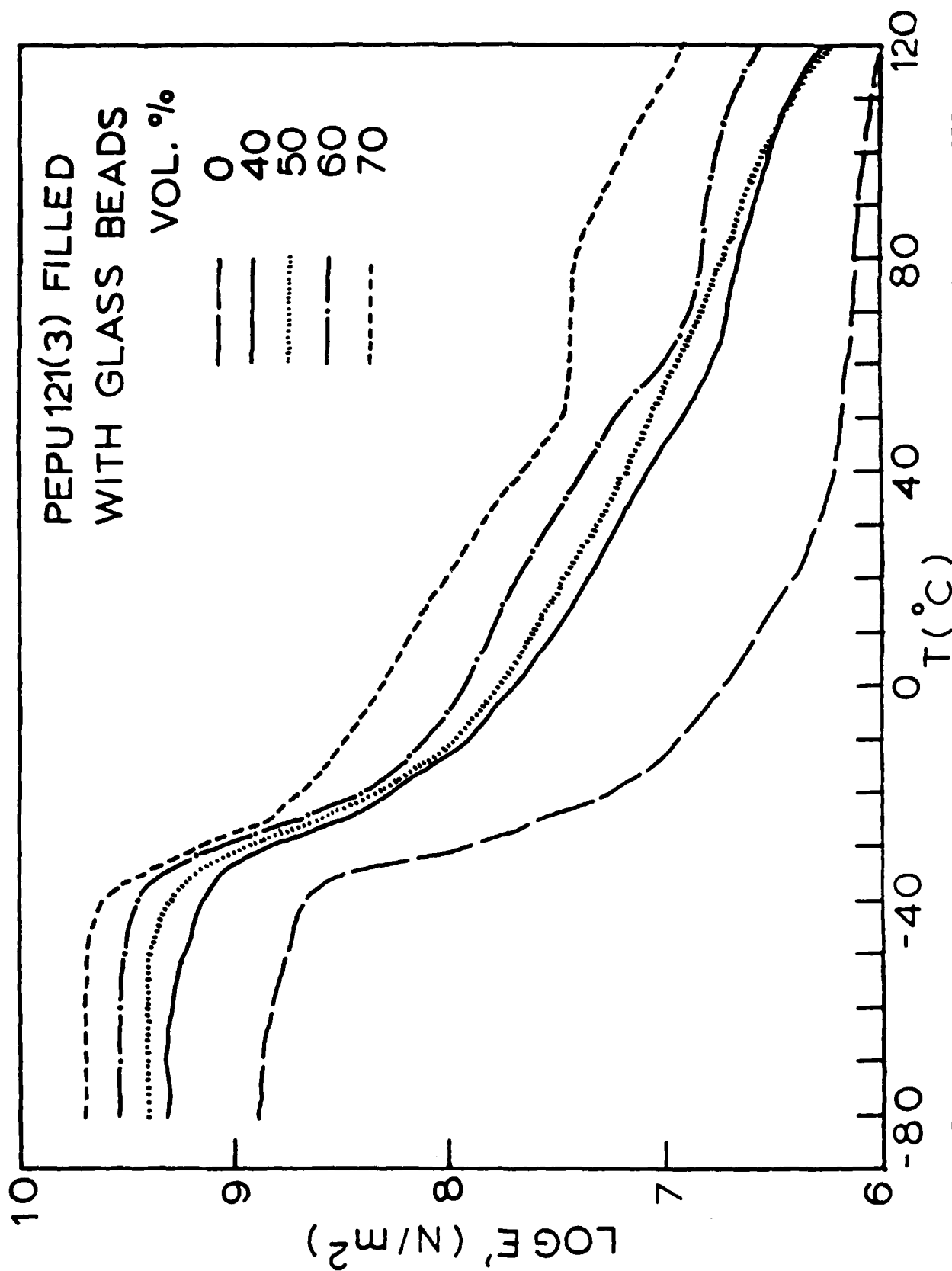


FIGURE 3.9. DMTA ANALYSIS FOR PEPU Bi 121 FILLED WITH GLASS BEADS AT DIFFERENT CONCENTRATIONS.

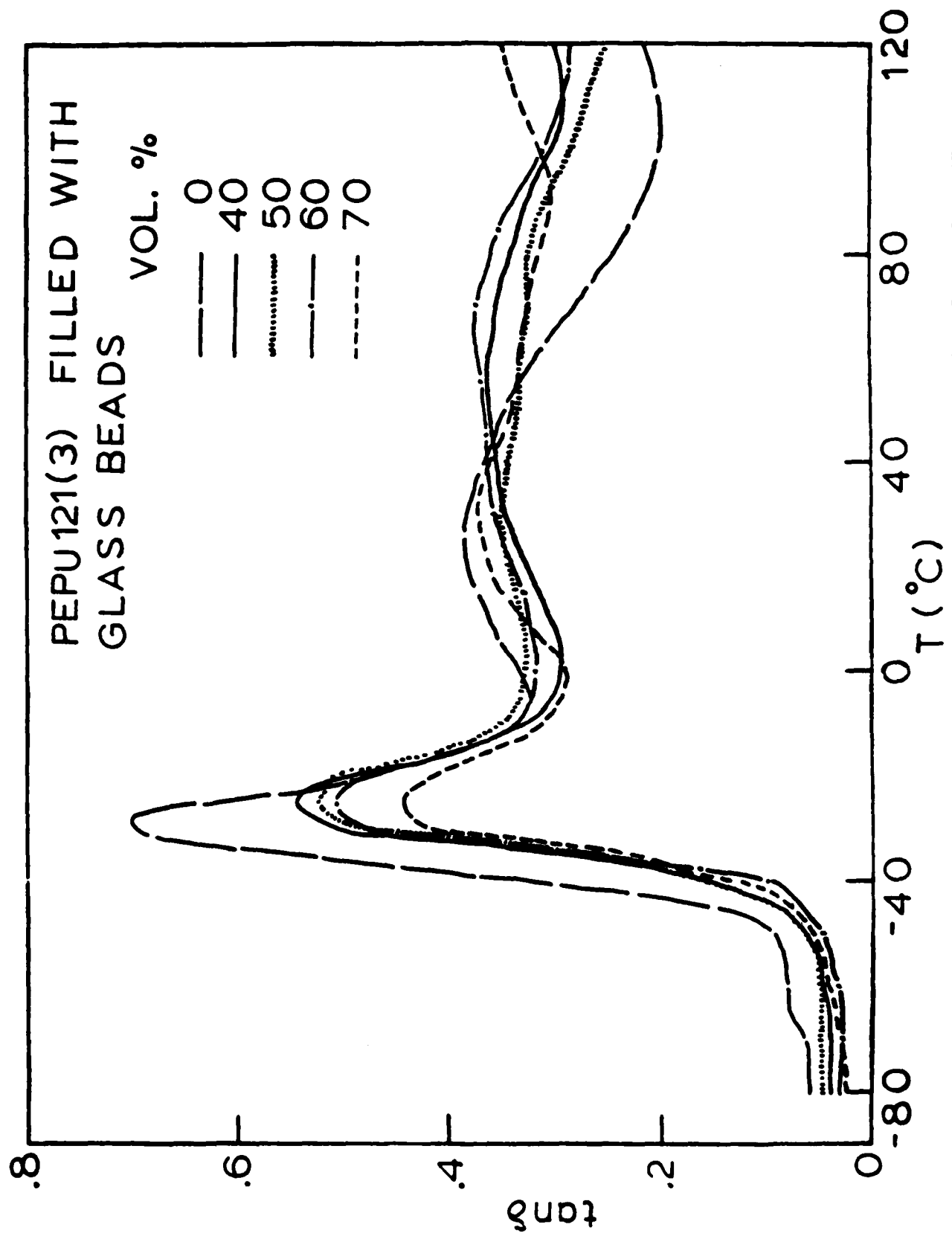


FIGURE 3.10. DMTA ANALYSIS FOR PEPU B1 121 FILLED WITH GLASS BEADS AT DIFFERENT CONCENTRATIONS.

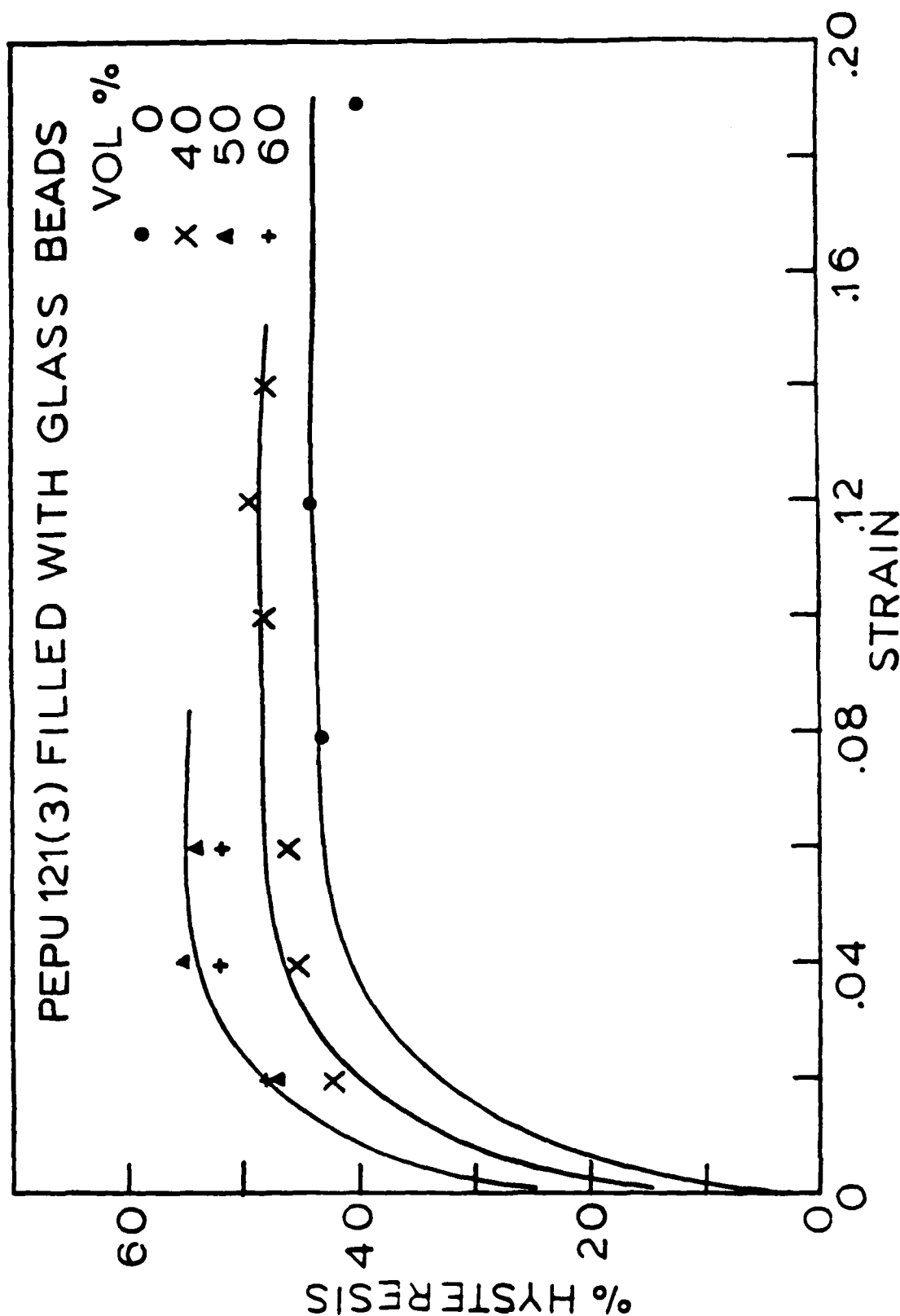


FIGURE 3.11. HYSTERESIS VS. STRAIN . PEPU B1 121 FILLED WITH GLASS BEADS AT DIFFERENT CONCENTRATIONS.

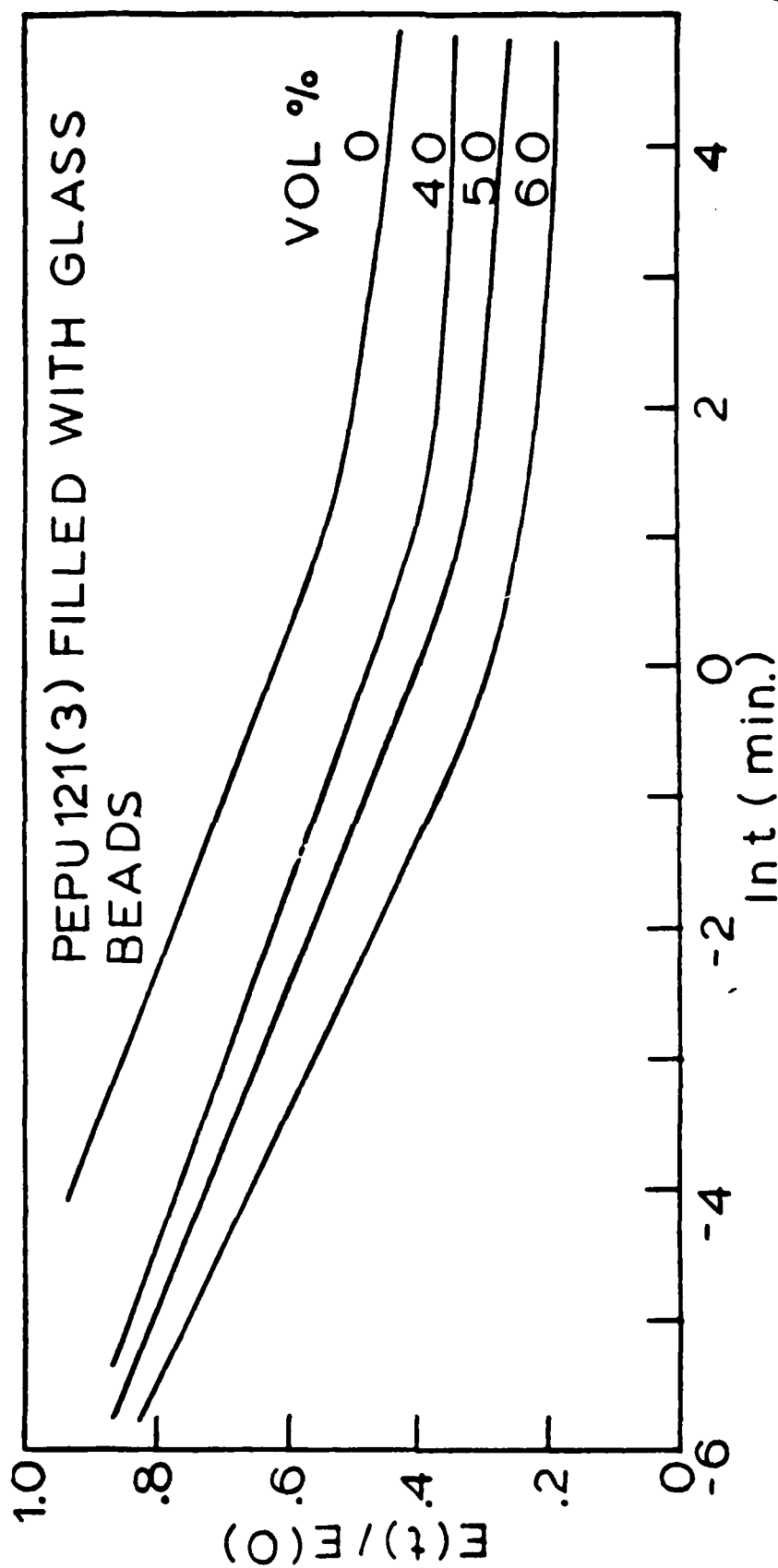


FIGURE 3.12. TENSILE RELAXATION. RELATIVE MODULUS VS. TIME FOR PEPU B1 121 FILLED WITH GLASS BEADS AT DIFFERENT CONCENTRATIONS.

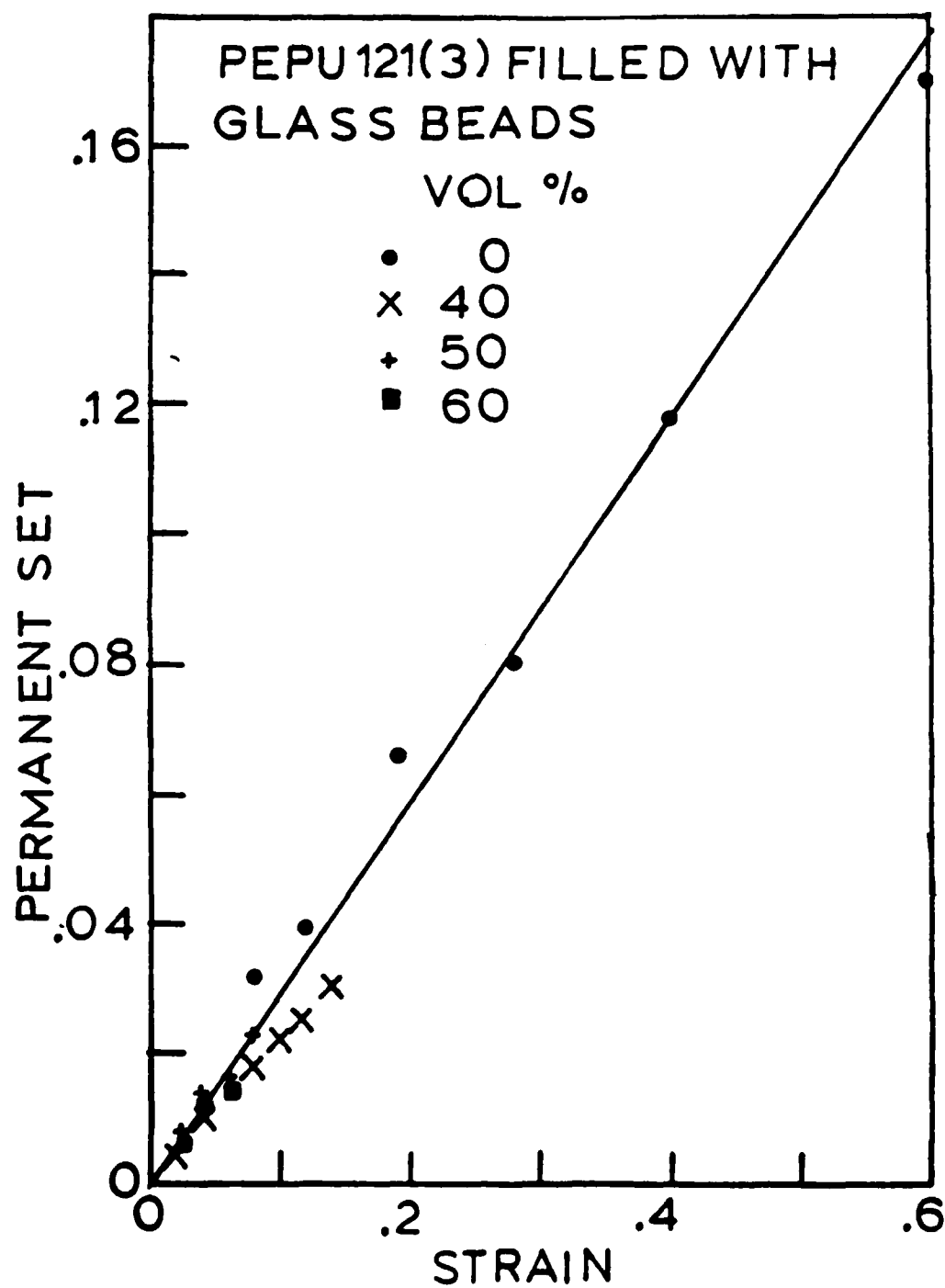


FIGURE 3.13. PERMANENT SET VS. STRAIN FOR PEPU B1 121
FILLED WITH GLASS BEADS AT DIFFERENT
CONCENTRATIONS.

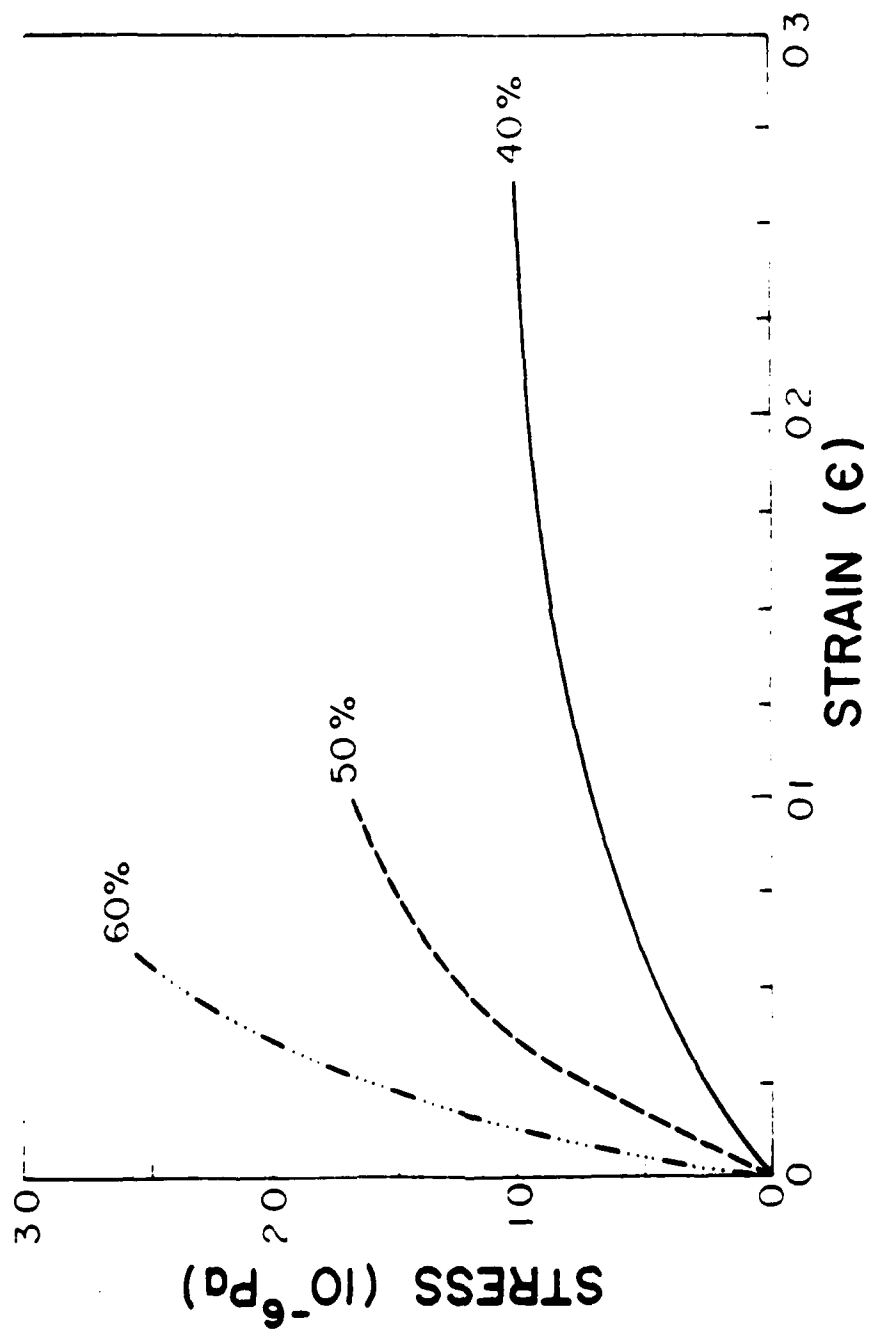


FIGURE 3 14 STRESS-STRAIN TENSILE TEST PEPU Bi 121
FILLED WITH CaCO_3 ($\dot{\epsilon} = 1 \text{ cm/min}$)

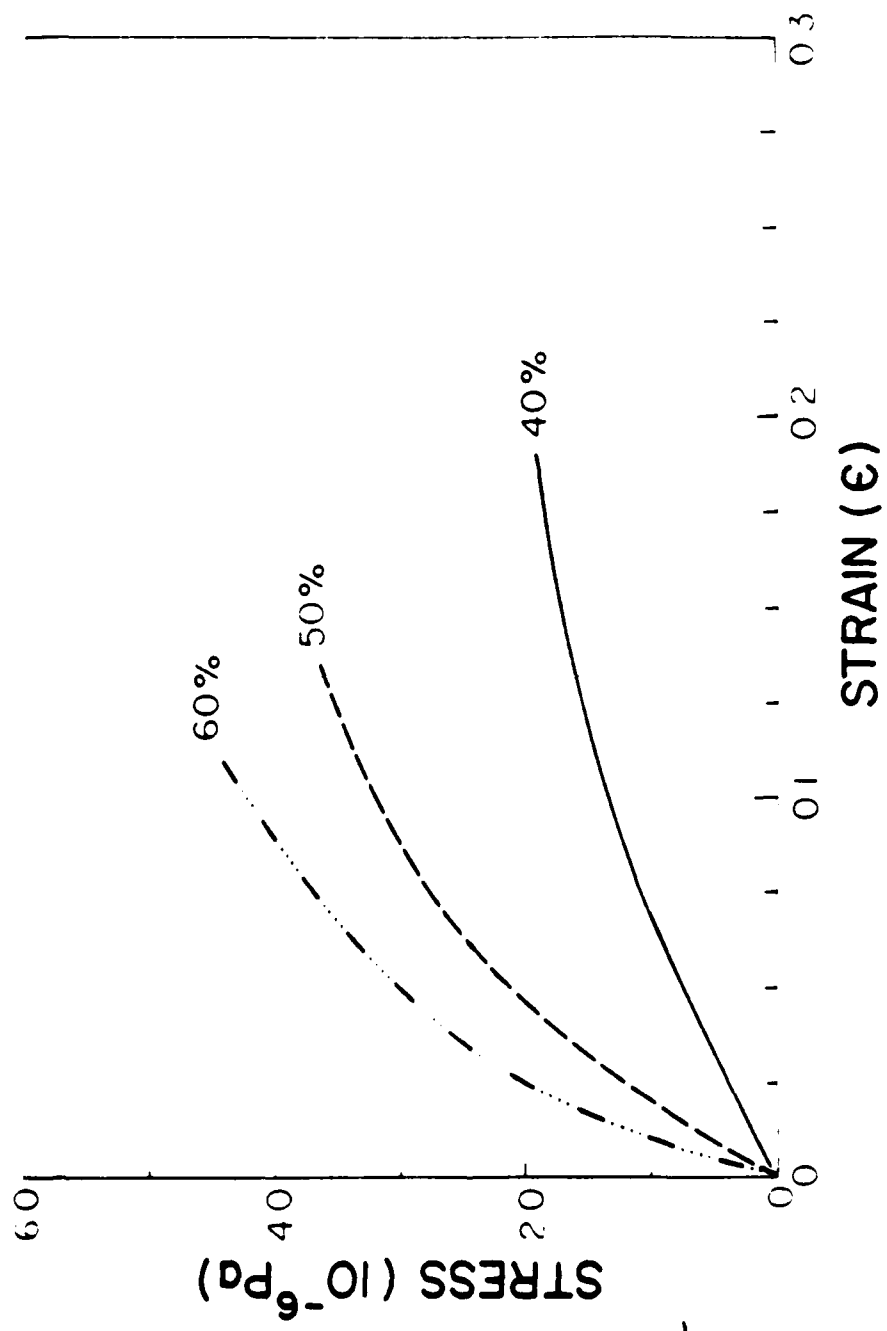


FIGURE 3 15 COMPRESSION TESTS FOR PEPU B1 121 FILLED WITH CaCO_3 ($\dot{\epsilon} = 1 \text{ cm/min}$)

TABLE 3.7. TENSILE AND COMPRESSION TEST RESULTS FOR
CaCO₃ FILLED PEPU-121

TENSILE TEST			
PEPU 121 + CaCO ₃	$E \times 10^{-6} \text{ Pa}$	ϵ_b	$\sigma_b \times 10^{-6} \text{ Pa}$
40%	13.1	0.26	1.0
50%	31.2	0.10	1.6
60%	75.0	0.06	2.6
Compression			
PEPU 121 + CaCO ₃	$E \times 10^{-6} \text{ Pa}$	ϵ_b	$\sigma_b \times 10^{-6} \text{ Pa}$
40%	15.8	0.19	1.95
50%	50.0	0.19	3.7
60%	100.0	0.11	4.45

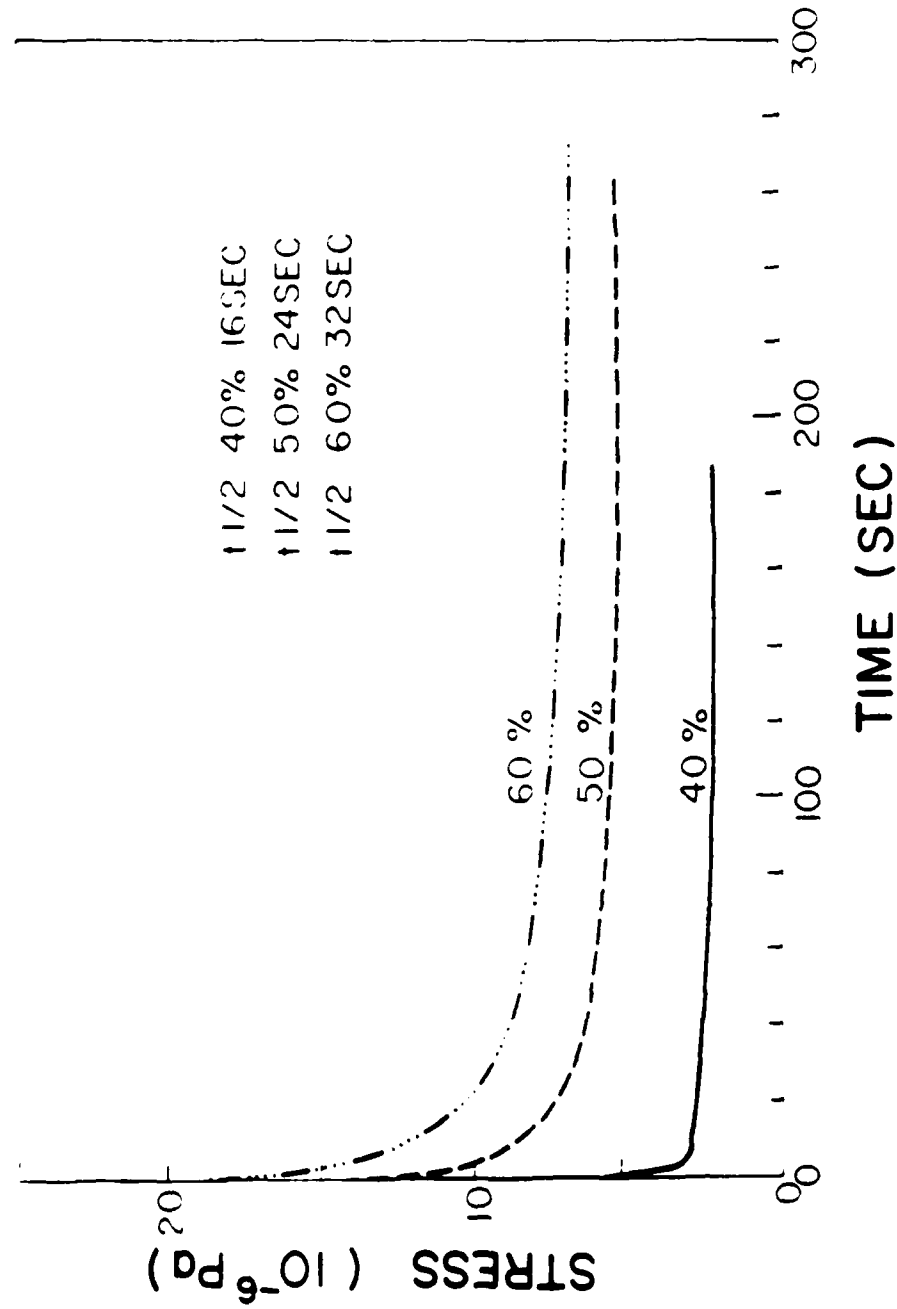


FIGURE 3 16 TENSILE RELAXATION TEST PEPU B1 I2I FILLED WITH CaCO_3 AT DIFFERENT CONCENTRATIONS (INITIAL DEFORMATION 4%)

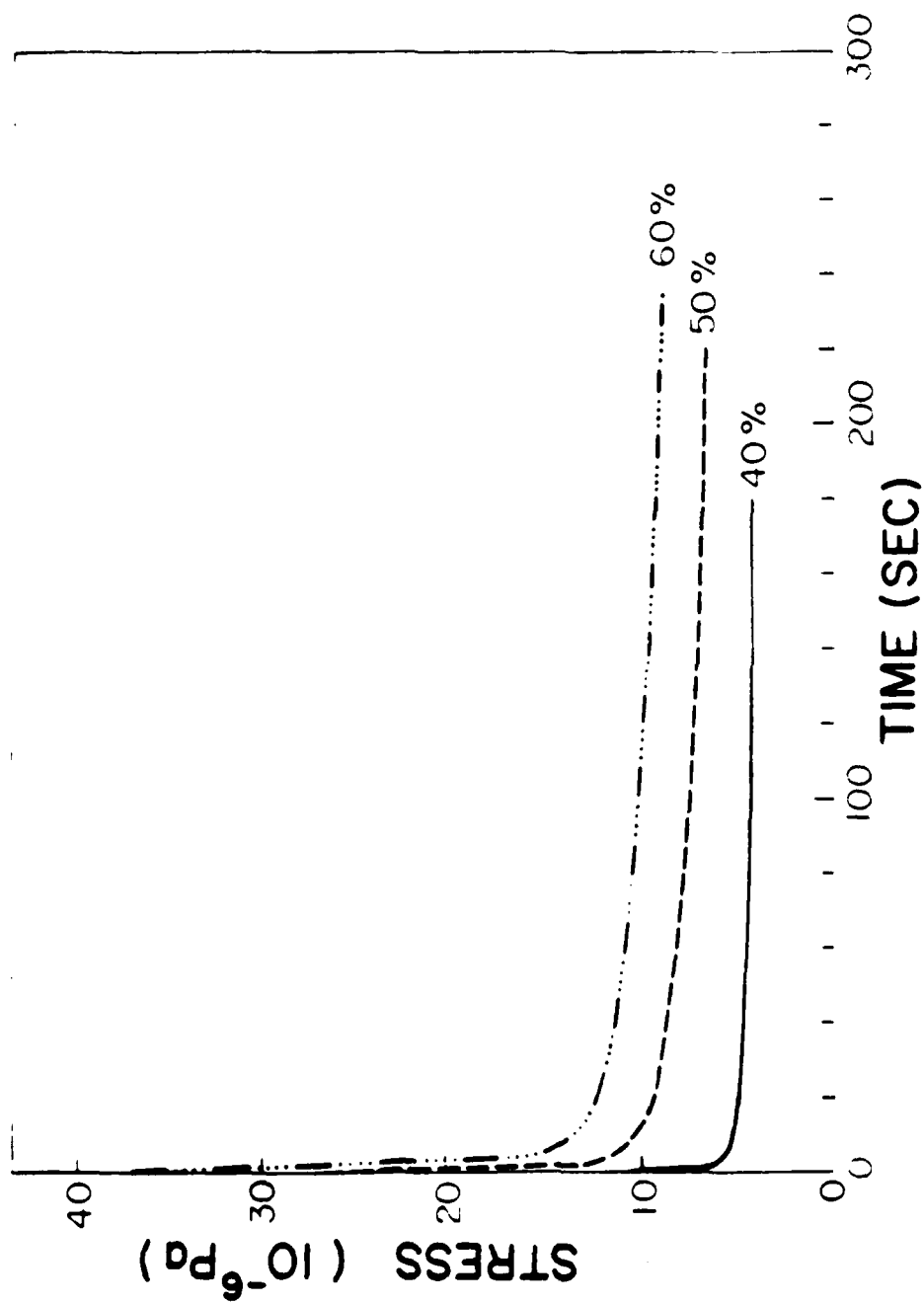


FIGURE 3 17 COMPRESSION-RELAXATION TESTS PEPU B1 I2I
FILLED WITH CaCO_3 AT DIFFERENT CONCENTRA
TIONS (INITIAL DEFORMATION 5%)

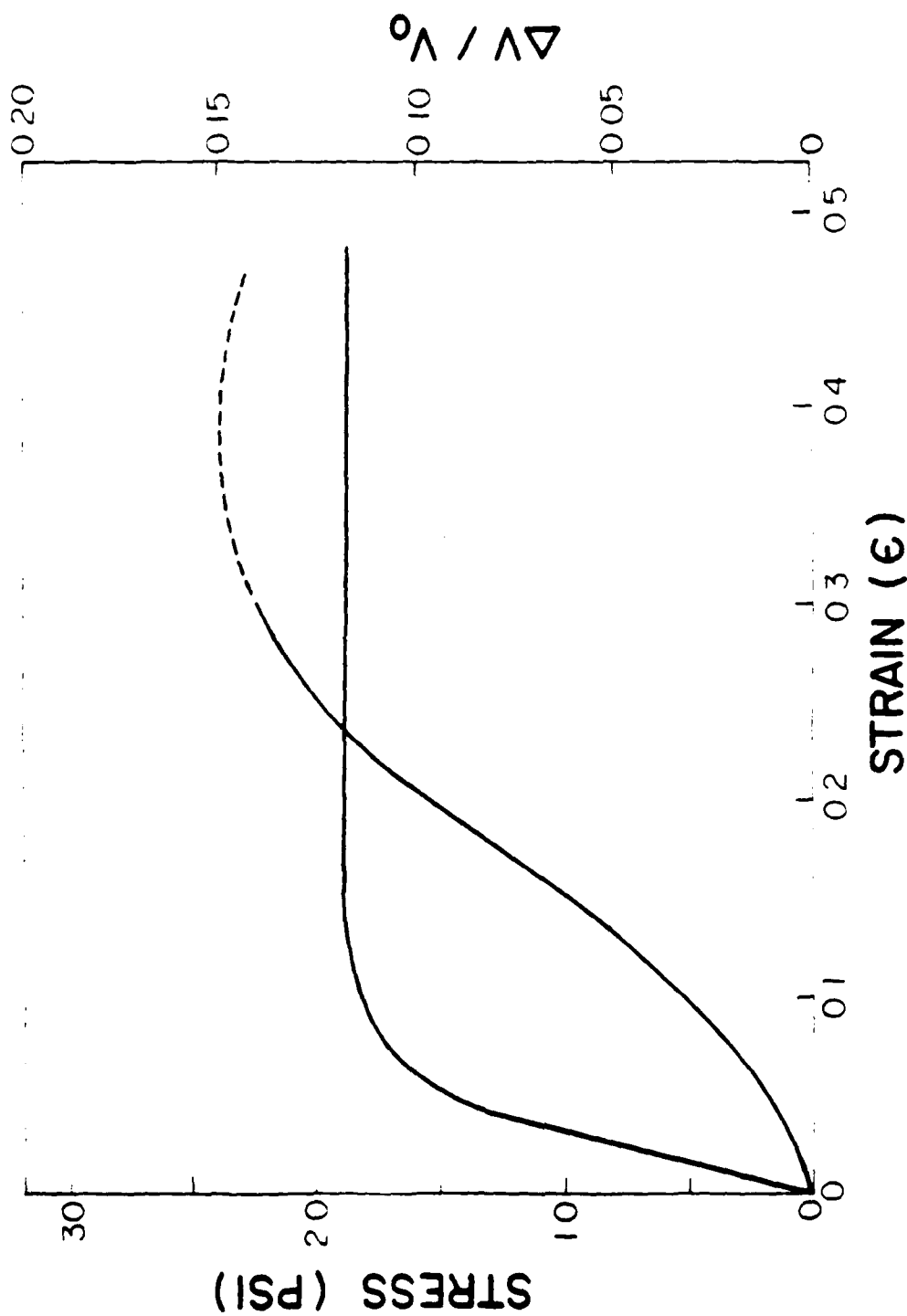


FIGURE 318 STRESS-STRAIN-DILATATION TEST FOR PEPU R1121
 FILLED WITH GLASS BEADS (40%), MOLDED 80C
 ($\dot{\epsilon} = 4 \text{ cm/min}$)

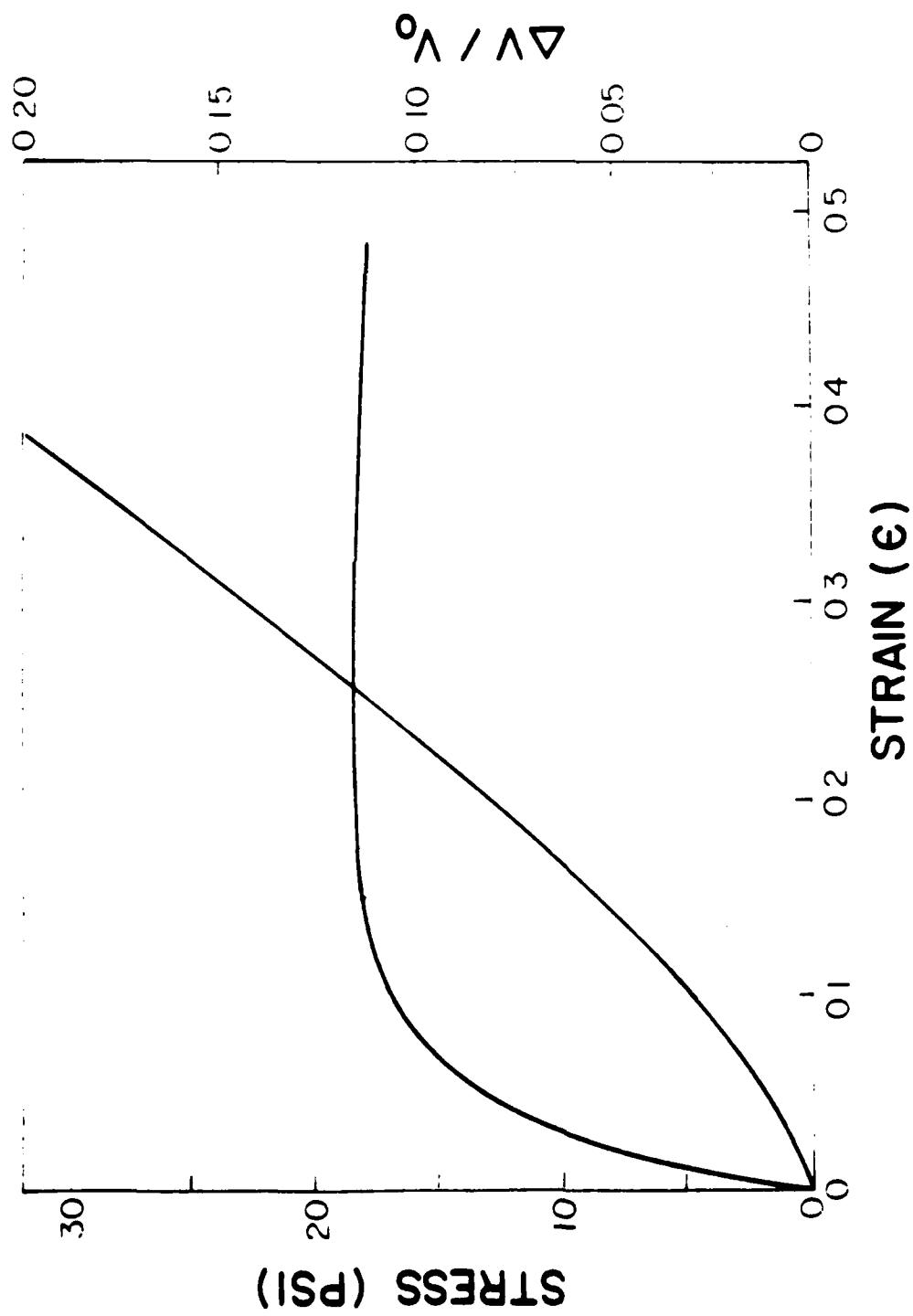


FIGURE 3 19 STRESS - STRAIN - DILATATION FOR PEPU Bi 121 FILLED WITH GLASS BEADS (40%), MOLDED 90C ($\dot{\epsilon} = 4\text{cm/min}$)

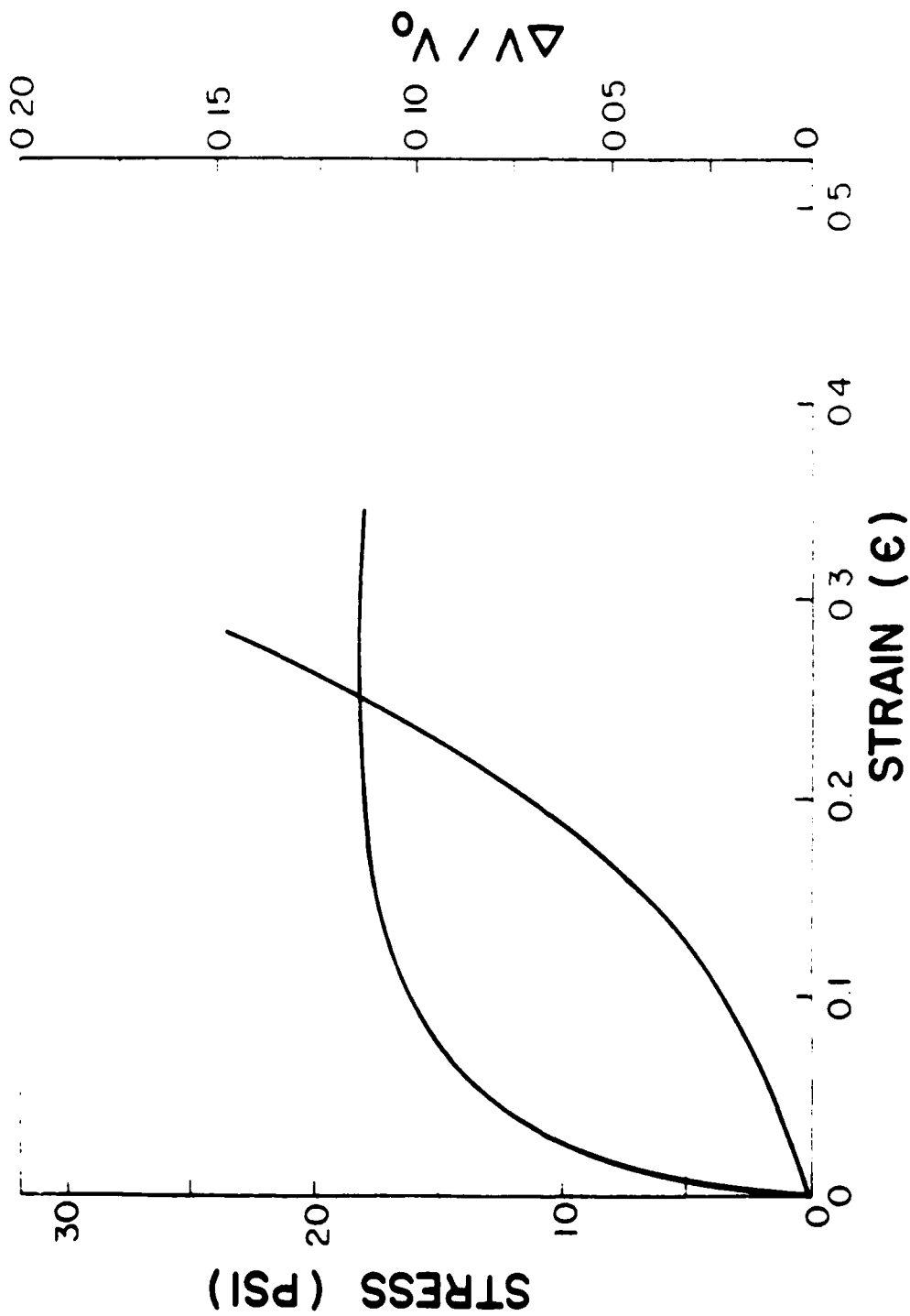
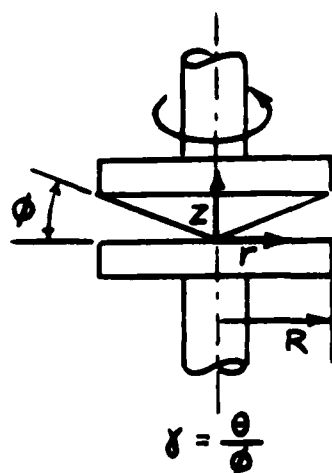
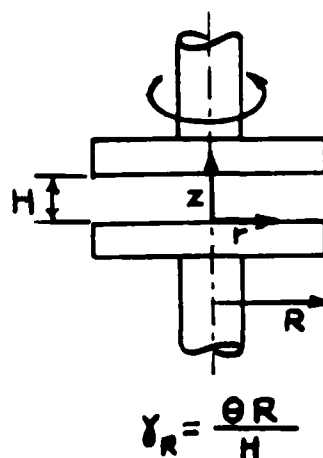


FIGURE 3 20 STRESS-STRAIN-DILATATION TEST FOR PEPU B1 I2I
 FILLED WITH GLASS BEADS (40%), MOLDED 100 C
 ($\dot{\epsilon} = 4 \text{ cm/min}$)

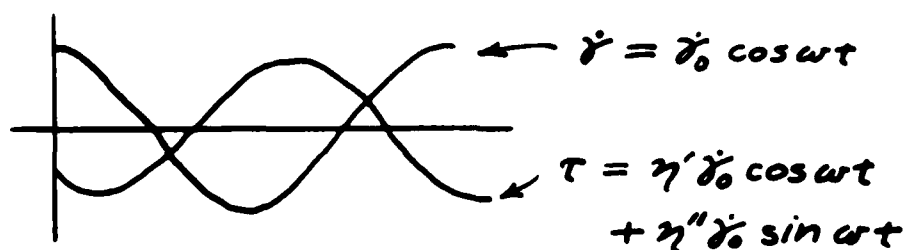
Cone and Plate



Parallel Disk



Oscillatory shear :



$$G'' = \omega \eta', \quad \text{loss modulus}$$

$$G' = \omega \eta'', \quad \text{storage modulus}$$

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2}, \quad \text{complex viscosity}$$

Figure 4.1. Characterization in oscillatory shear.

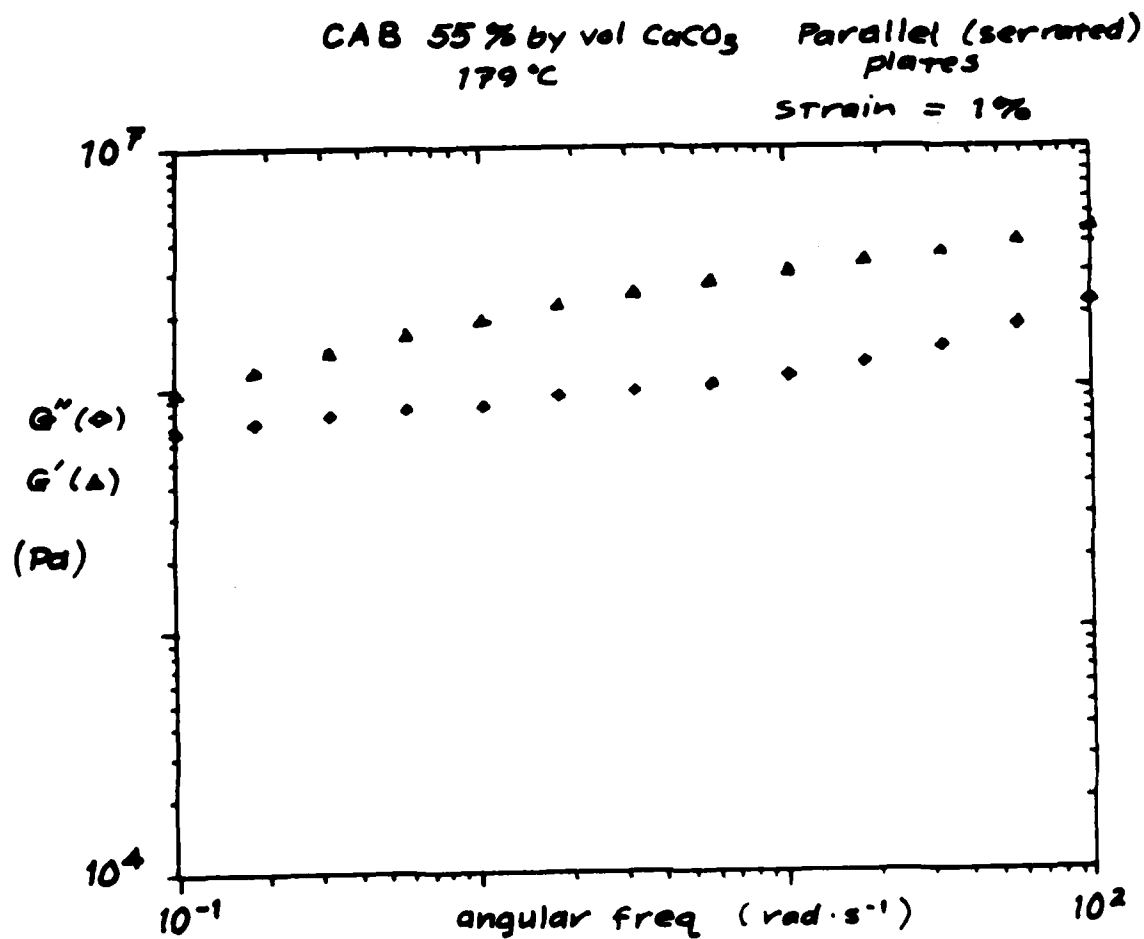
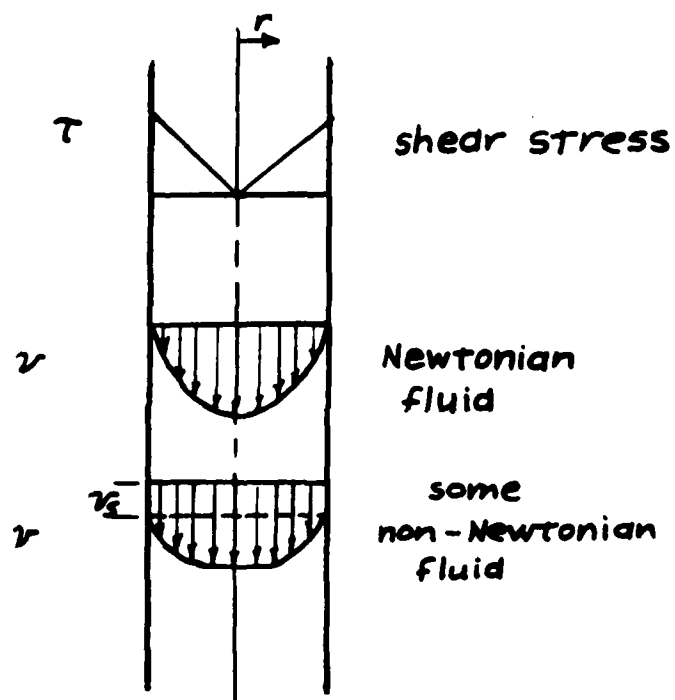


Figure 4.2. Strain dependence of complex modulus of CAB with 55 vol. % filler (CaCO_3).

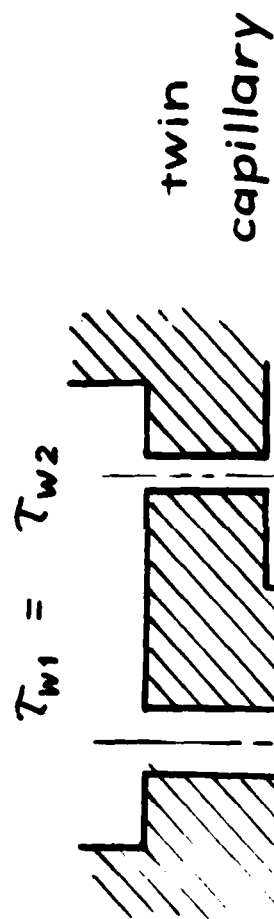
Flow through a capillary



$$\tau_w = \frac{R}{2} \frac{\Delta P}{L}$$

Figure 4.4. Stress and velocity in capillary flow with wall slip.

$$\tau_w = \frac{R \Delta P}{2L}, \quad \frac{Q}{\pi R^3} = \frac{v_s}{R} + \frac{1}{\tau_w^3} \int_0^{\tau_w} \tau^2 \dot{\gamma} d\tau$$



$$v_s = \frac{\frac{Q_1}{\pi R_1^3}}{\frac{1}{R_1} - \frac{1}{R_2}} \frac{Q_2}{\pi R_2^3}$$

Figure 4.5. Twin-capillary for the measurement of wall slip.

Figure 4.6. Temperature sweep of complex modulus of several LOVA binder candidates as polymerized at UMass.

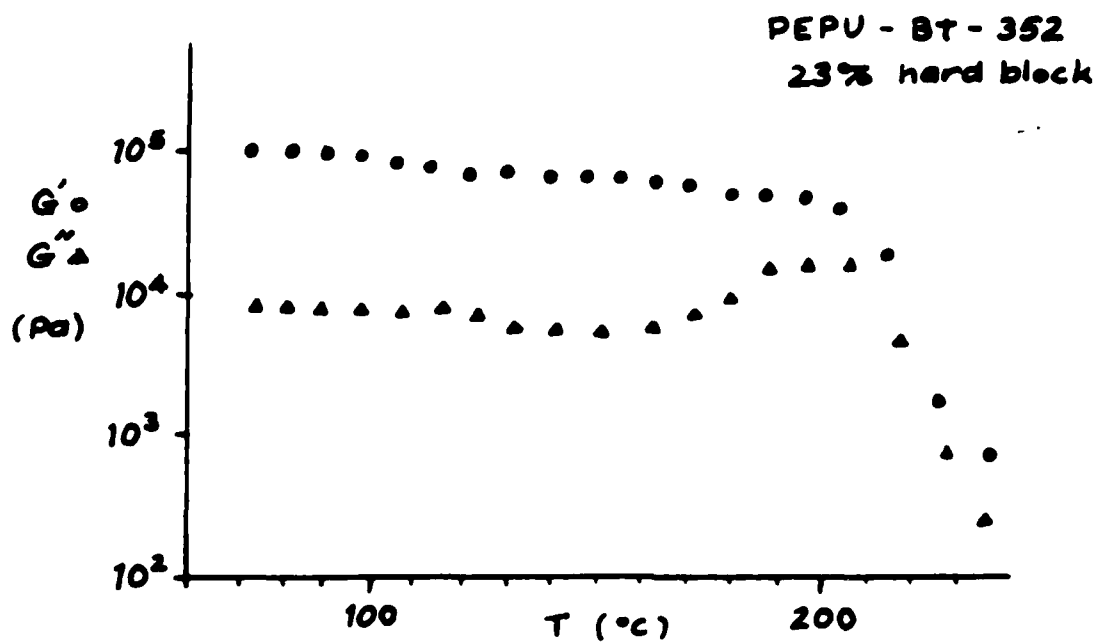


Figure 4.6a

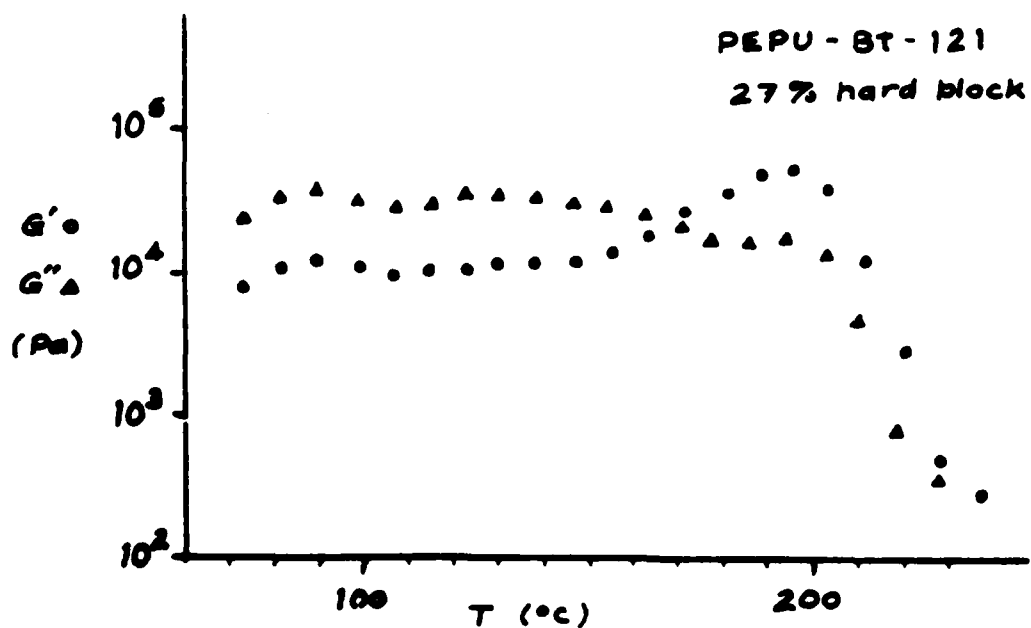


Figure 4.6b

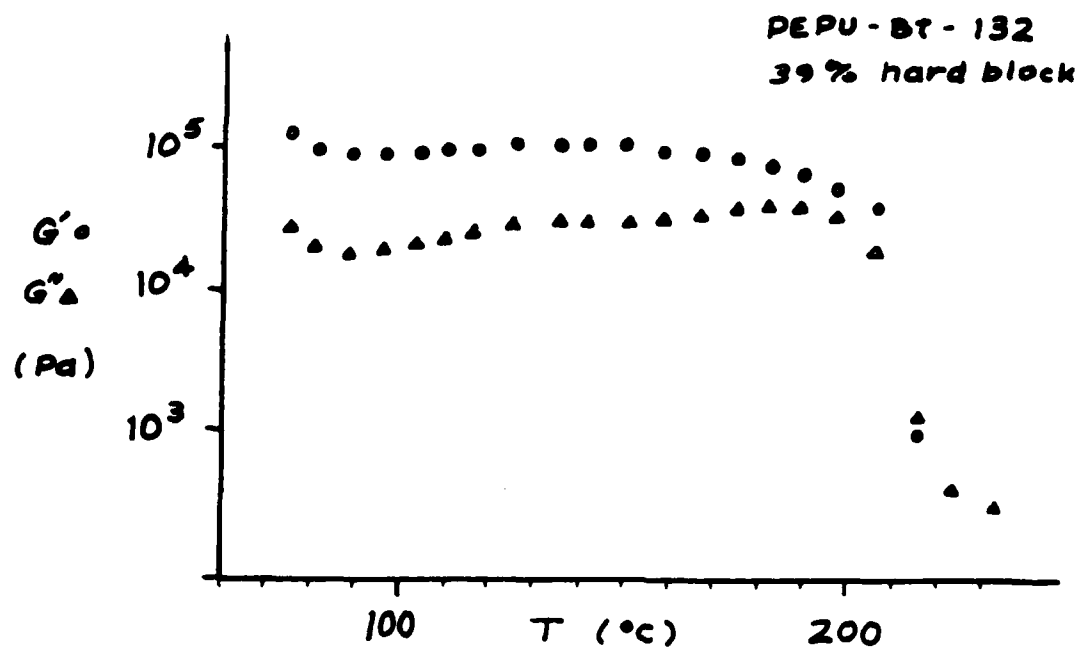


Figure 4.6c

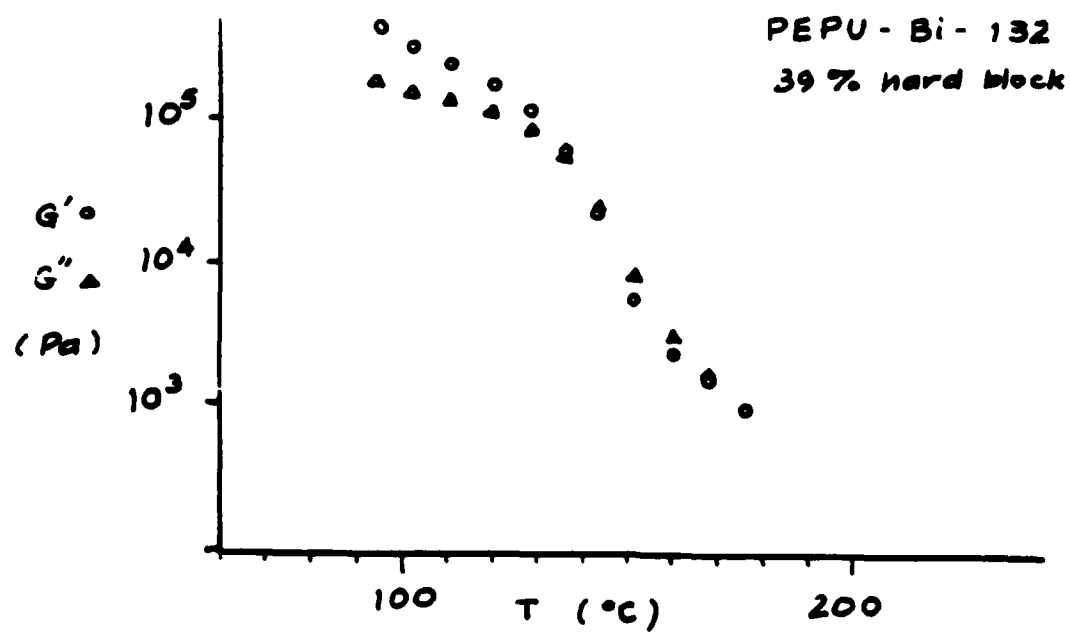


Figure 4.6d

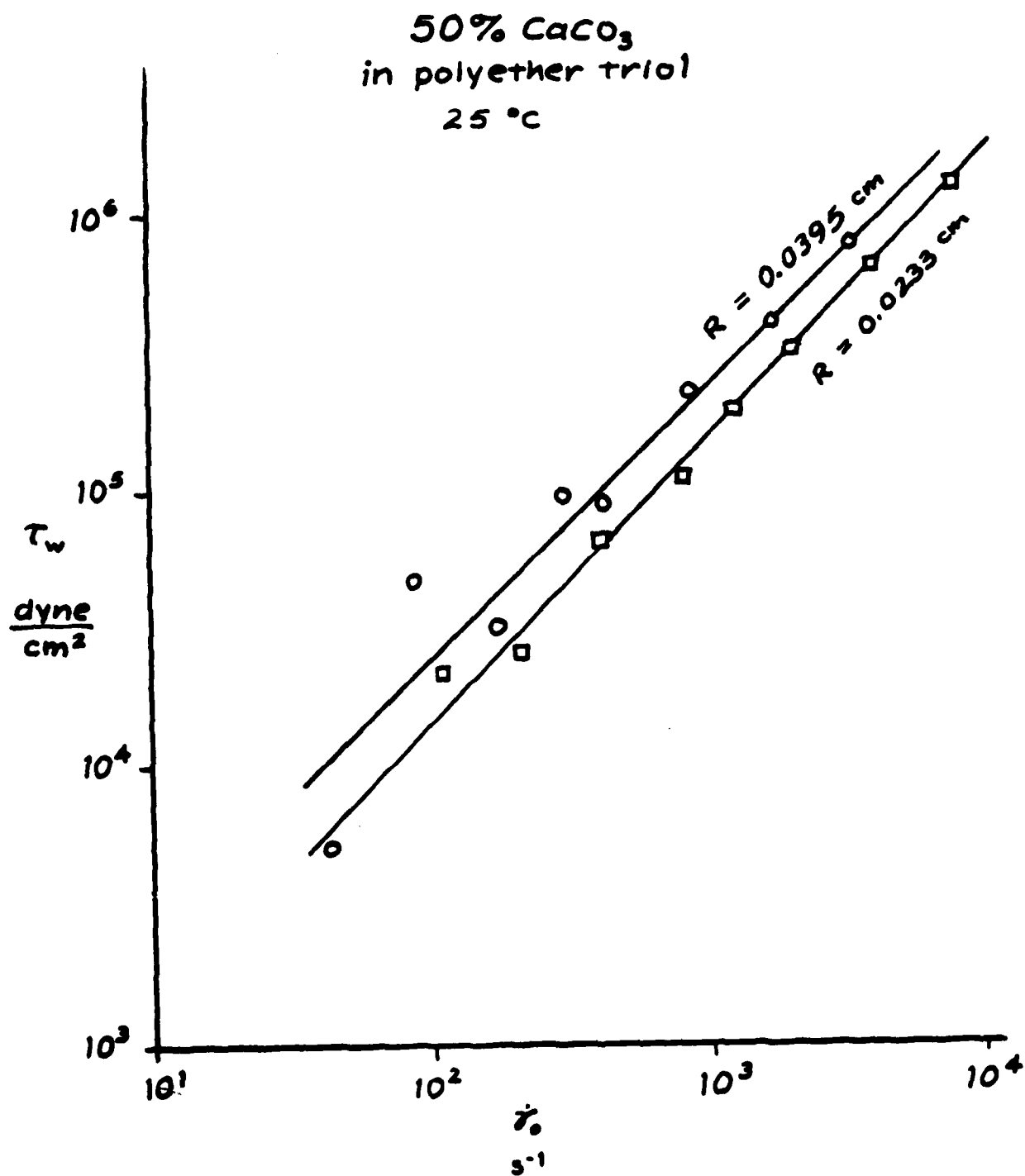


Figure 4.7. Wall shear stress as a function of shear rate for capillary flow with slip at the wall.

Steady shear viscosity
50 % CaCO_3 in polyether triol, 25°C

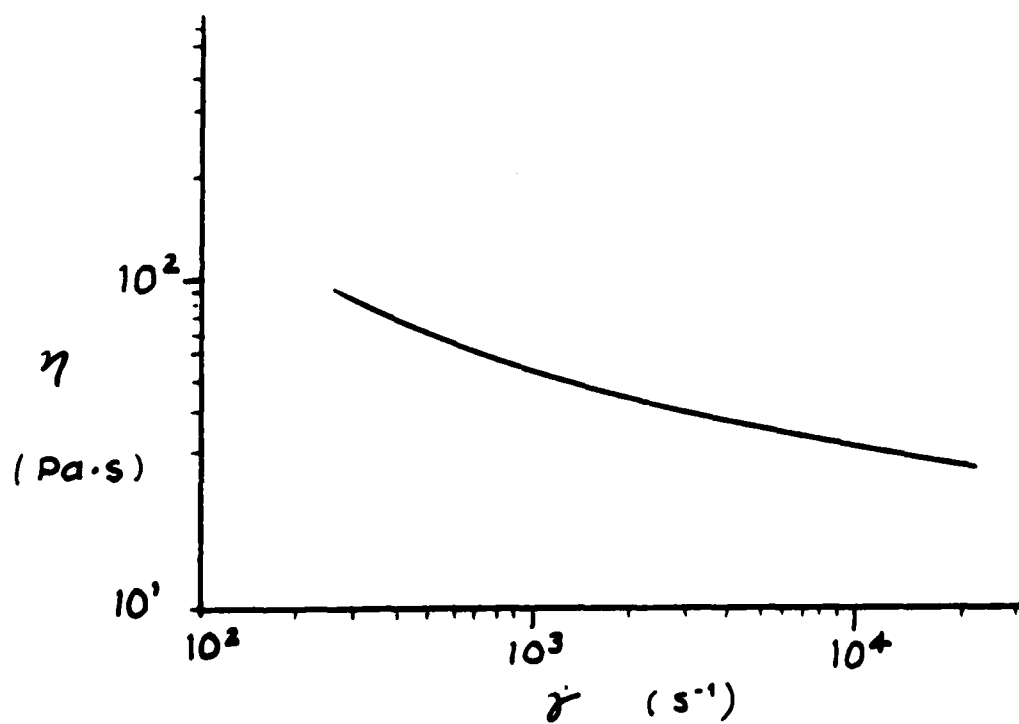


Figure 4.8. Steady shear viscosity of polyether triol with 50 vol. % CaCO_3 , at 25°C.

Slip velocity vs. shear stress
50% CaCO_3 in polyether triol
25°C

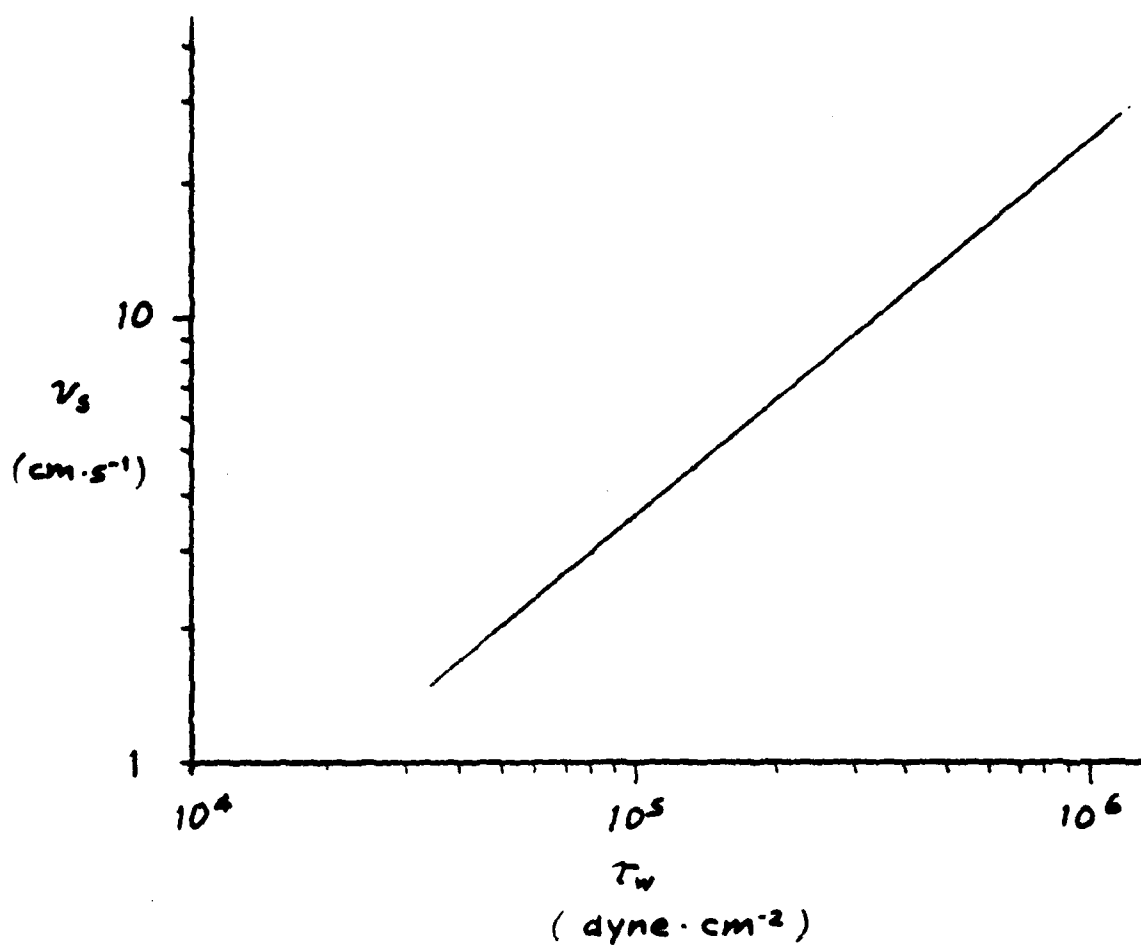


Figure 4.9. Slip velocity as a function of the shear stress at the wall.

PDMS/CaCO₃ (50 vol%) 30°C

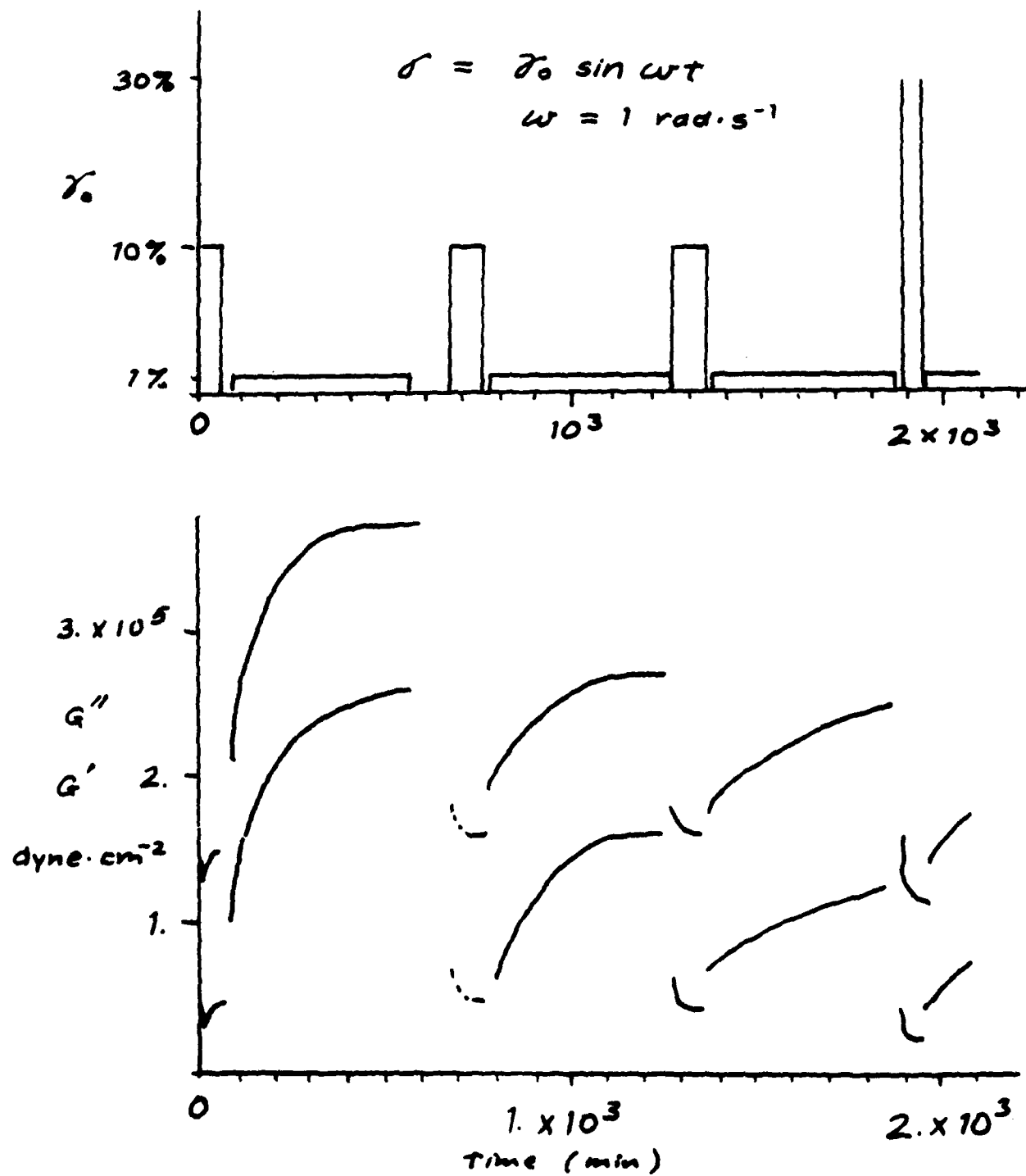


Figure 4.10

PDMS 50 vol% CaCO_3 24°C
Equibiaxial start-up

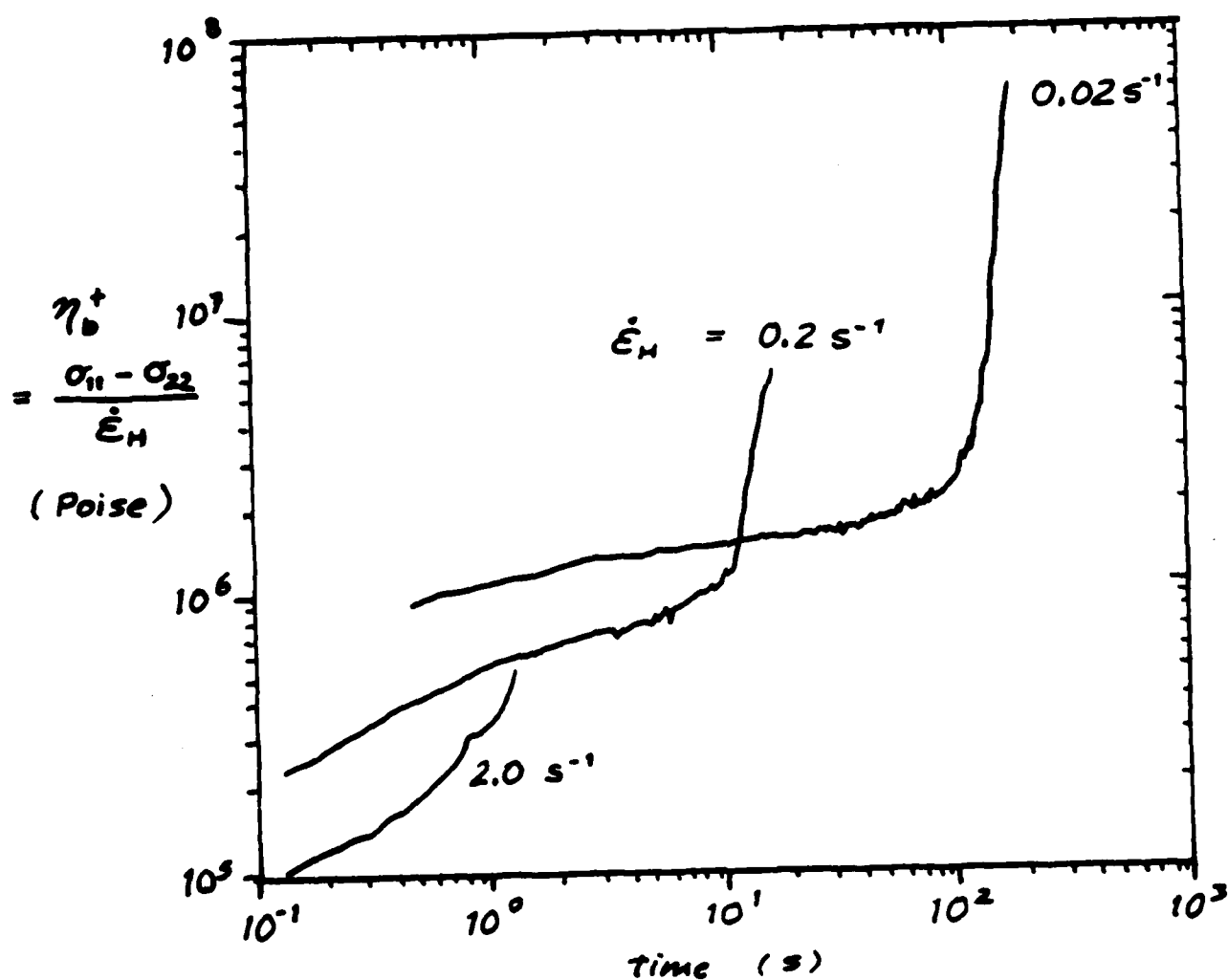
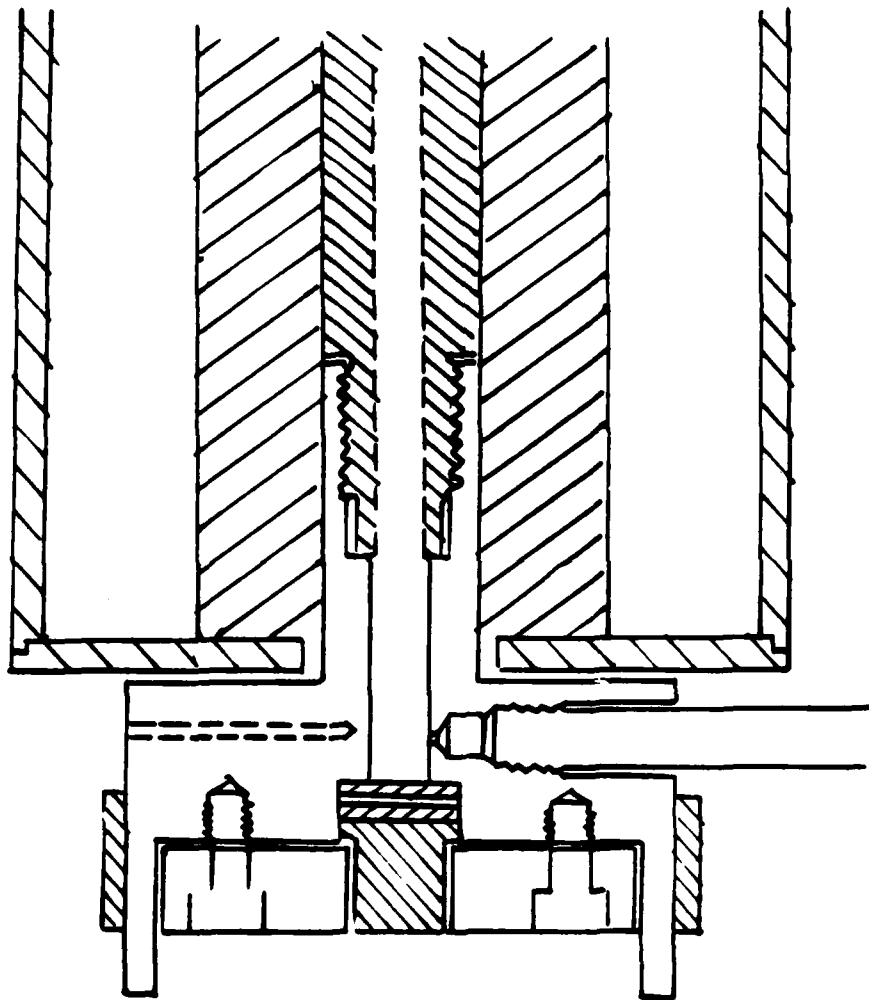


Figure 4.11. Stress development in start-up of extensional flow at constant rate.

47-



EXTRUSION SET-UP

Figure 4.12. Sketch of ram extruder and gun propellant die as used at UMass.

PEPU-Bi-121 50% CaCO_3
100 °C

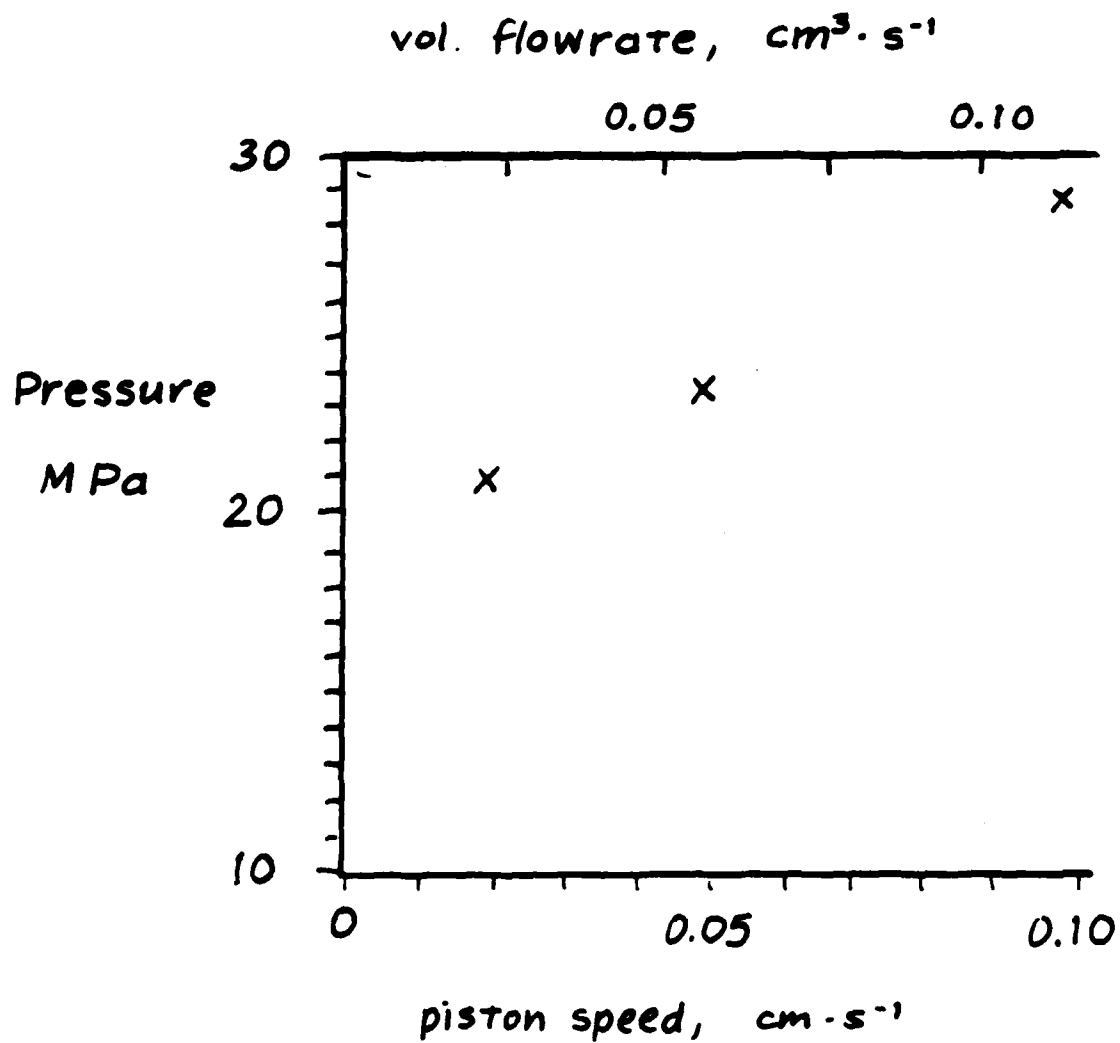
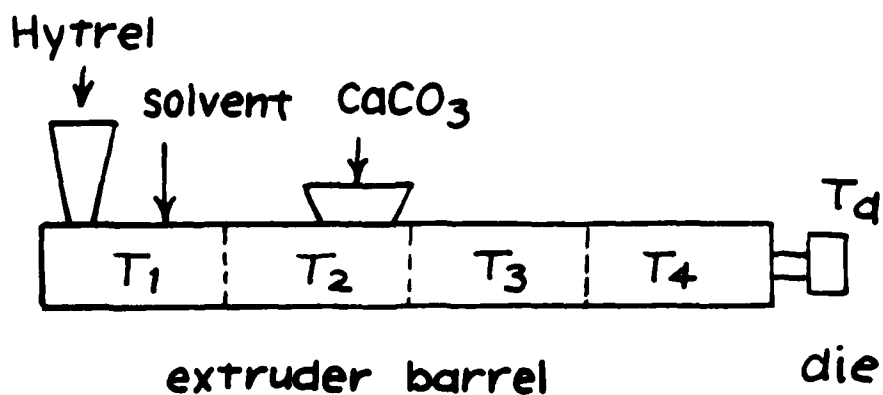


Figure 4.13. Extrusion pressure for ram extrusion of PEPU (Bi 1-2-1) through gun propellant die.



Feed rates:	Hytrel	solvent	CaCO ₃
(lb/hr)	4.0	2.0	13.8

Temperatures:	T ₁	T ₂	T ₃	T ₄	T _d
(°C)	120°	163°	140°	156°	180°

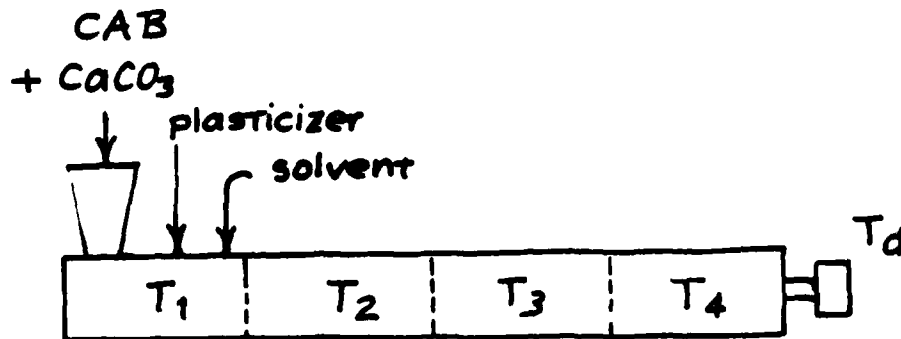
RPM = 100

Die pressure = 1500 - 2000 psi

Power consumption = 1.5 - 1.8 kW

Figure 4.14. Twin-screw processing conditions for highly filled Hytrel system.

4.15



Feed rates : CAB CaCO_3 plast. solv.
 2.3 11.9 1.14 < 0.5

Temperatures : T_1 T_2 T_3 T_4 T_d
 ($^{\circ}\text{C}$) 50° 50° 40° 40° 60°

RPM = 80

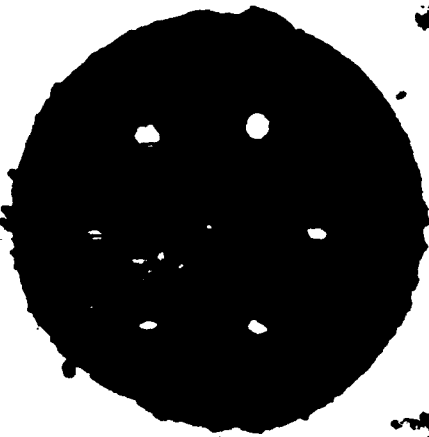
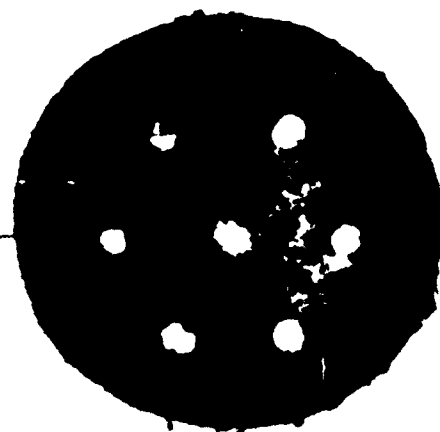
Die pressure = 800 psi

Power consumption = 1.45 kW

Figure 4.15. Twin-screw processing conditions for highly filled CAB system.

1. Hytrel CaCO_3	2. CAB sugar
3. CAB CaCO_3	

Figure 4.16. Extrudate cross-sections for twin-screw extruder experiments.



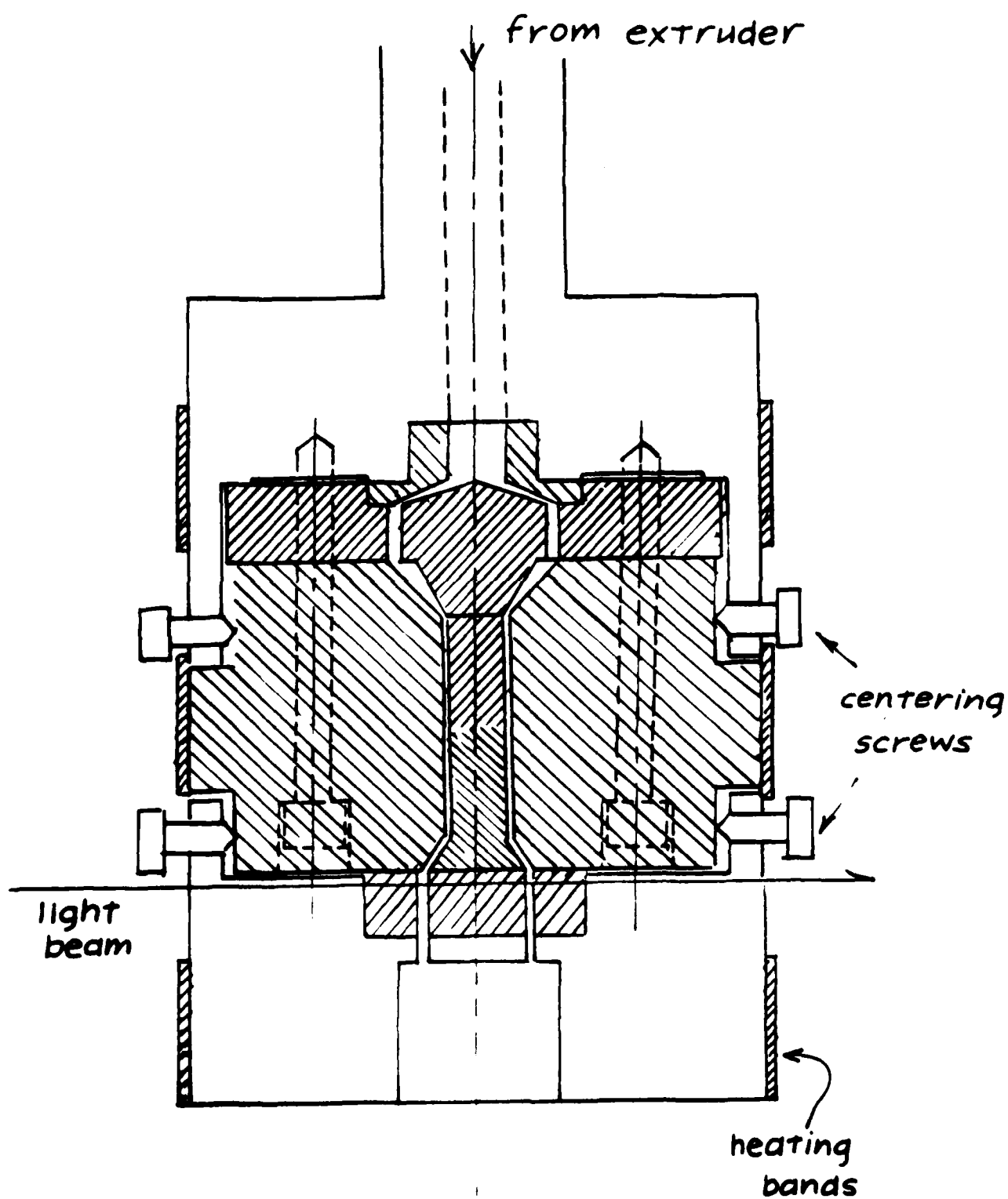


Figure 4.17. Annular extruder for optical stress measurements. The end section die is made of glass.

Figure Captions

- Figure 4.1: Rheological characterization in oscillatory shear.
- Figure 4.2: Strain dependence of complex modulus of CAB with 50 vol% filler (CaCO_3).
- Figure 4.3: Sketch of ram extruder which is used as capillary rheometer.
- Figure 4.4: Stress and velocity in capillary flow with wall slip.
- Figure 4.5: Twin-capillary for measurement of wall slip.
- Figure 4.6: Temperature sweep of complex modulus of several LOVA binder candidates as polymerized at UMass.
- Figure 4.7: Wall shear stress as a function of shear rate for capillary flow with slip at the wall.
- Figure 4.8: Steady shear viscosity of polyether triol with 50 vol% CaCO_3 , at 25°C .
- Figure 4.9: Slip velocity as a function of the shear stress at the wall.
- Figure 4.10: Transient structuring behavior of highly filled system as observed in oscillatory shear at small strain amplitude, 1%, and large amplitude, 10%.
- Figure 4.11: Stress development in start-up of extensional flow at constant rate.
- Figure 4.12: Sketch of ram extruder and gun propellant die as used at UMass.
- Figure 4.13: Extrusion pressure for ram extrusion of PEPI (Bi 1-2-1) through gun propellant die.
- Figure 4.14: Twin-screw processing conditions for highly filled Hytrel system.
- Figure 4.15: Twin-screw processing conditions for highly filled CAB system.

Figure 4.16: Extrudate cross-sections for twin-screw extruder experiments.

Figure 4.17: Annular extrusion die for optical stress measurements. The end section of the die is made of glass.