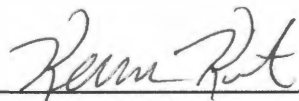


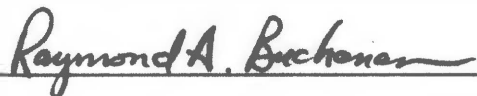
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I am submitting herewith a thesis written by Nicolas Conte entitled "Dynamic Mechanical Characterization of Very Soft Polymeric Materials Using Nanoindentation Techniques." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Materials Science and Engineering.


George Pharr, Major Professor

We have read this thesis and
recommend its acceptance:





Acceptance for the Council:


Vice Provost and Dean of
Graduate Studies

**DYNAMIC MECHANICAL CHARACTERIZATION
OF VERY SOFT POLYMERIC MATERIALS
USING NANOINDENTATION TECHNIQUES**

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

**Nicolas Conte
May 2002**

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ACKNOWLEDGMENTS

There are many people I would like to thank for contributing to the completion of this thesis.

I would like to begin by thanking my excellent advisor, Dr. George Pharr, for the opportunity to further my education and for his positive approach and invaluable guidance. I would also like to thank the other members of my committee, Dr. Raymond Buchanan and Dr. Kevin Kit, for their time and patience in review of this work.

I am grateful to Dr. Kevin Kit for giving me the opportunity to use the DMA Rheometric ScientificTM instrument, as well as the advice he has offered me.

Last, I would like to thank MTS Systems Corporation, my current employer, for assisting me. I wish to thank Dr. Vincent Jardret and Dr. Warren Oliver for helping me with the development of this research.

ABSTRACT

Polymer thin films and surfaces play a major role in the functionality of many components in the microelectronic and automotive industries. The characterization of their mechanical properties at a nanometer scale remains a technological challenge. Depth-sensing indentation, with frequency-specific dynamic analysis, provides means for viscoelastic measurement of near surface properties of polymeric materials. The development of new automated test methodologies with improved measurement accuracy and precision for evaluating very soft polymeric materials are presented in this work. Results of viscoelastic properties at various frequencies for polyurethane and polydimethylsiloxane, using both Berkovich and Flat punch geometries, are compared. Indentation results are compared to the results of dynamic mechanical analysis testing on the same materials.

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NOMENCLATURE

Symbols

A : projected area

B : constant

b : sample geometry

C : measured damping

C_c : contact damping

C_i : damping of the instrument

D : diameter of the flat punch indenter

E : Young's modulus or elastic modulus

E' : storage modulus

E'' : loss modulus

E_i : elastic modulus of the indenter

E_r : reduced modulus

f : frequency

F : harmonic load

f_o : force amplitude

F_o : harmonic load amplitude

G^* : complex modulus

H : hardness

h : static displacement

h_c : contact depth

h_f : final displacement

h_{max} : maximum penetration

k : displacement amplitude

K : measured stiffness

K_f : frame stiffness

K_s : stiffness of the instrument (spring stiffness)

m : indenter mass / constant

$m_1, \dots, m_5$: constant

n : stress exponent

P : static load

S : contact stiffness

t : time

$\tan \delta$: loss tangent or tangent delta

z : harmonic displacement

z_o : harmonic displacement amplitude

ΔL : elongation of the sample

δ : phase angle for DMA

ε : constant for indentation / strain for DMA

ε_d : dynamic strain

ε_o : strain amplitude

ε_s : static strain

$\dot{\varepsilon}_i$: indentation strain rate

$\dot{\varepsilon}$: strain rate

ϕ : phase angle for indentation

γ^* : complex strain

ν : Poisson's ratio

ν_i : Poisson's ratio of the indenter

σ^* : complex stress

σ : stress

σ_d : dynamic stress

σ_o : stress amplitude

σ_s : static stress

ω : angular frequency

Abbreviations

CSM: Continuous Stiffness Measurement

DMA: Dynamic Mechanical Analysis

DMTA: Dynamic Mechanical Thermal Analyser

DSI: Depth Sensing Indentation

PDMS: Polydimethylsiloxane

PU: Polyurethane

CHAPTER 1 INTRODUCTION

The purpose of this study was to improve the understanding of how frequency-specific depth sensing indentation techniques can be used to measure the viscoelastic properties of materials. The techniques for measurement of time dependent mechanical properties can be divided into two classes: (1) broad-band, quasi-static or creep techniques, and (2) frequency-specific dynamic techniques. While standard bulk testing techniques exist for these types of measurements, in many instances the volumes of material of interest may be on such a scale that bulk techniques become impractical. Such is the case for thin film devices found in many different fields in development. Thus, a considerable effort has been devoted recently to the investigation of the mechanical properties of thin films. One of the most promising techniques for measuring the mechanical properties of solids, on a spatially resolved basis, is depth-sensing indentation (DSI) [1, 2, 3]. An important alternative to traditional DSI is offered by dynamic measurement techniques, also known as frequency-specific DSI (CSM technique) [1, 4]. Both static and dynamic mechanical properties can be measured using this technique. Recently, it was shown that it is possible to measure linear viscoelastic properties of a solid polymer using this technique [5, 6].

Since the first quantitative results for measuring the viscoelastic properties using frequency-specific DSI [5, 6], a limited amount of work has been done. The first goal of this work was to develop a new automated test methodology, by which one can measure the viscoelastic properties of very soft polymeric materials at various frequencies using frequency-specific DSI. This test methodology has been applied for two different indenter tip geometries: the Berkovich triangular pyramid and a flat circular punch. The new methodology is based on improvements to the measurement accuracy and precision of the

frequency-specific DSI technique and to automated instrument calibration over a range of frequency. The technique is used to measure the viscoelastic properties of two soft polymeric materials, a polyurethane and a polydimethylsiloxane, using two indenter tip geometries (Berkovich and flat punch). The second goal of the work was to compare the indentation results with those of a bulk dynamic mechanical testing technique, Dynamic Mechanical Analysis (DMA) [7, 8].

CHAPTER 2 REVIEW OF LITERATURE

2.1 ELASTIC-PLASTIC INDENTATION

Boussinesq [9] and Hertz [10] originally considered the elastic contact problem in the late 19th century. Boussinesq developed a method based on potential theory for computing the stresses and displacements in an elastic body loaded by a rigid, axisymmetric indenter. Hertz analyzed the problem of elastic contact between two spherical surfaces with different radii and elastic modulus. Another major contribution was made by Sneddon [11, 12], who derived general relationships among the load, displacement, and contact area for any indenter that can be described as a solid of revolution of a smooth function. Modeling indentation contact in a way that includes plasticity is a much more complex problem. Therefore, an understanding of plasticity in indentation contact problems has been derived largely through experimentation and finite element simulation.

The two mechanical properties measured most frequently by DSI methods are hardness, H , and elastic modulus (Young's modulus), E . A simple methodology has been developed, by which these properties can be determined for isotropic materials exhibiting no time dependence in their deformation behavior, that is, no creep or viscoelasticity [2, 3]. A schematic illustration of the indentation process for an axisymmetric indenter of arbitrary profile is shown in Figure 1. As the indenter is driven into the material, both elastic and plastic deformation processes occur, producing a hardness impression that conforms to the shape of the indenter to some contact depth, h_c . As the indenter is withdrawn, only the elastic portion of the displacement is recovered, which effectively allows

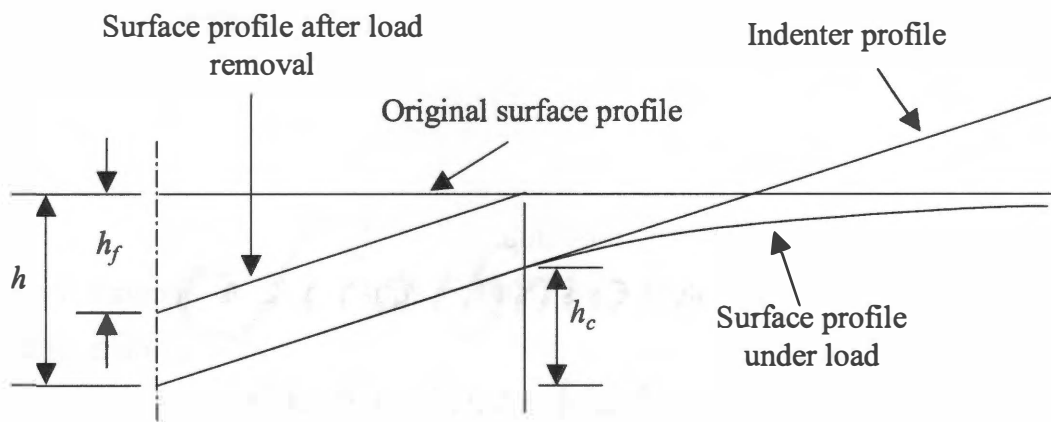


Figure 1. A schematic illustration of the indentation process for an axisymmetric indenter of arbitrary profile.

one to separate the elastic properties of the material from the plastic. A schematic representation of the indentation load versus displacement data, obtained during one full cycle of loading and unloading, is presented in Figure 2. The hardness and the elastic modulus are derived from the contact stiffness, S , using the fundamental relations:

$$H = \frac{P}{A} \quad (1)$$

where P is the load and A is the projected contact area at that load, and:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (2)$$

where E_r is the reduced elastic modulus.

The reduced modulus, E_r , is used in equation (2) to account for the fact that elastic displacement occurs in both the indenter and the sample. The elastic modulus of the test material, E , is calculated from E_r using:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (3)$$

where ν is Poisson's ratio for the test material, and E_i and ν_i are, respectively, the elastic modulus and Poisson's ratio of the indenter.

From equations (1) and (2), it is clear that in order to calculate the hardness and the elastic modulus from indentation load-displacement data, one must have an accurate measurement of the contact stiffness and the projected contact area under load. The most widely used method for establishing the contact area was developed by Oliver and Pharr [2]. This method begins by

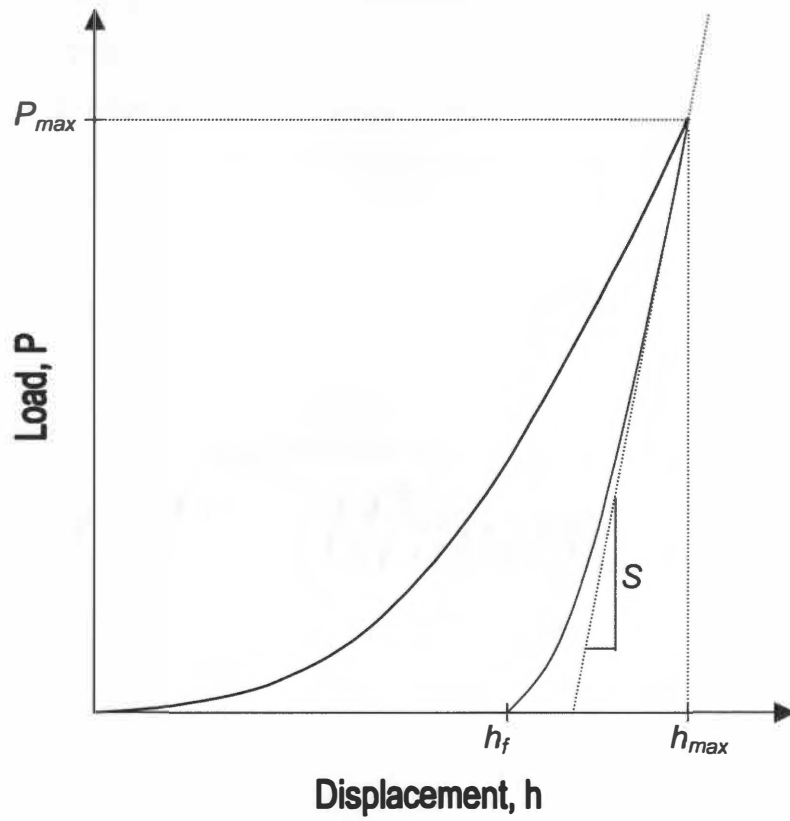


Figure 2. A schematic representation of the indentation load (P) versus displacement (h) data obtained during one full cycle of loading and unloading.

fitting the unloading portion of the load-displacement data to the power-law relation:

$$P = B(h - h_f)^m \quad (4)$$

where B and m are empirically determined fitting parameters, and h_f is the final displacement after complete unloading, also determined from the curve fit. The contact stiffness, S , is established by analytically differentiating equation (4) and evaluating the result at the maximum depth of penetration, $h=h_{max}$, that is:

$$S = \left(\frac{dP}{dh} \right)_{h=h_{max}} = Bm(h_{max} - h_f)^{m-1} \quad (5)$$

The next step in the procedure is to estimate the contact depth, h_c , which for elastic contact is less than the total depth of penetration, h_{max} , as illustrated in Figure 1. The contact depth is estimated using:

$$h_c = h - \varepsilon \frac{P}{S} \quad (6)$$

where ε is a constant that depends on the indenter geometry. It has been shown that for spherical indenters $\varepsilon=0.75$, for conical indenters $\varepsilon=0.72$, and for flat punch indenters, $\varepsilon=1$ [2].

As a last step in the analysis, the projected contact area is calculated by evaluating an empirically determined indenter area function, A , at the contact depth h_c [2]; that is:

$$A = f(h_c) \quad (7)$$

2.2 INDENTATION OF MATERIALS WITH TIME DEPENDENT PROPERTIES

In the previous section, the indentation of elastic-plastic materials was introduced. Now, another behavior is considered: that of viscous deformation and creep. One of the techniques for measuring time dependent plastic phenomena is the creep technique described by the equation

$$\dot{\epsilon} = A\sigma^n \quad (8)$$

where $\dot{\epsilon}$ and σ are the strain-rate and stress, respectively, and n is the stress exponent. Furthermore, a technique for the measurement of viscoelastic time dependent phenomena is the dynamic mechanical technique described by the equation

$$\sigma^* = G^* \gamma^* \quad (9)$$

where σ^* is the complex stress, G^* is the complex modulus, and γ^* is the complex strain [8]. Time dependent deformation behavior strongly influences the shape of the load versus displacement curve, as shown in Figure 3. When the indenter is withdrawn from the surface after the initial loading, time-dependent deformation may still occur in the material, causing the indenter to further penetrate the specimen even when the applied load is decreasing. This results in a negative slope of the unloading curve. Clearly, time needs to be taken into account when analyzing the material response if viscoelasticity or creep are involved in the material deformation.

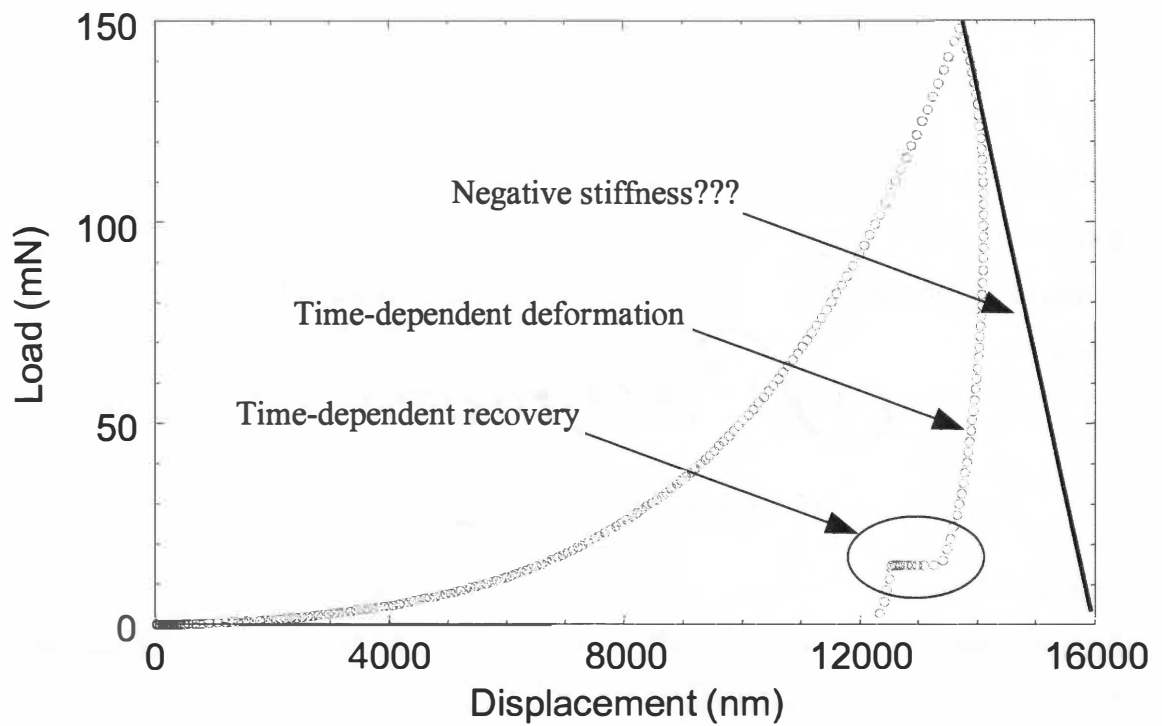


Figure 3. A plot of indentation load versus displacement for a material with a time dependent behavior.

2.2.1 FREQUENCY-SPECIFIC DSI (CSM TECHNIQUE)

An important alternative to traditional DSI is offered by dynamic measurement techniques, also known as frequency-specific DSI (CSM technique) [1, 4]. This technique involves adding a small harmonic force at a specific excitation frequency to the nominal force applied to the indenter, as shown in Figure 4, and analyzing the material's response to that harmonic force.

Figure 5 shows that a material exhibiting only elastic behavior has its displacement response in phase with the excitation force. However, if the behavior is viscoelastic, the displacement response lags behind the excitation force by a phase angle ϕ , as shown in Figure 6. This phase angle can vary from zero degree for purely elastic behavior to 90 degrees for purely viscous behavior. By measuring the amplitude of the resulting displacement and the phase lag between the excitation force and the displacement response, the contact stiffness and damping can be determined by

$$S = \frac{F_o}{z_o} \cos \phi \quad (10)$$

$$C_c \omega = \frac{F_o}{z_o} \sin \phi \quad (11)$$

where S is the contact stiffness, C_c is the contact damping, F_o is the amplitude of the harmonic load, and z_o is the amplitude of the harmonic displacement. Note that the dynamic characteristics of the measurement instrument must be taken into account in order to extract the contact stiffness, S , and damping, C_c , from the raw measurement data (see section 3.1.2).

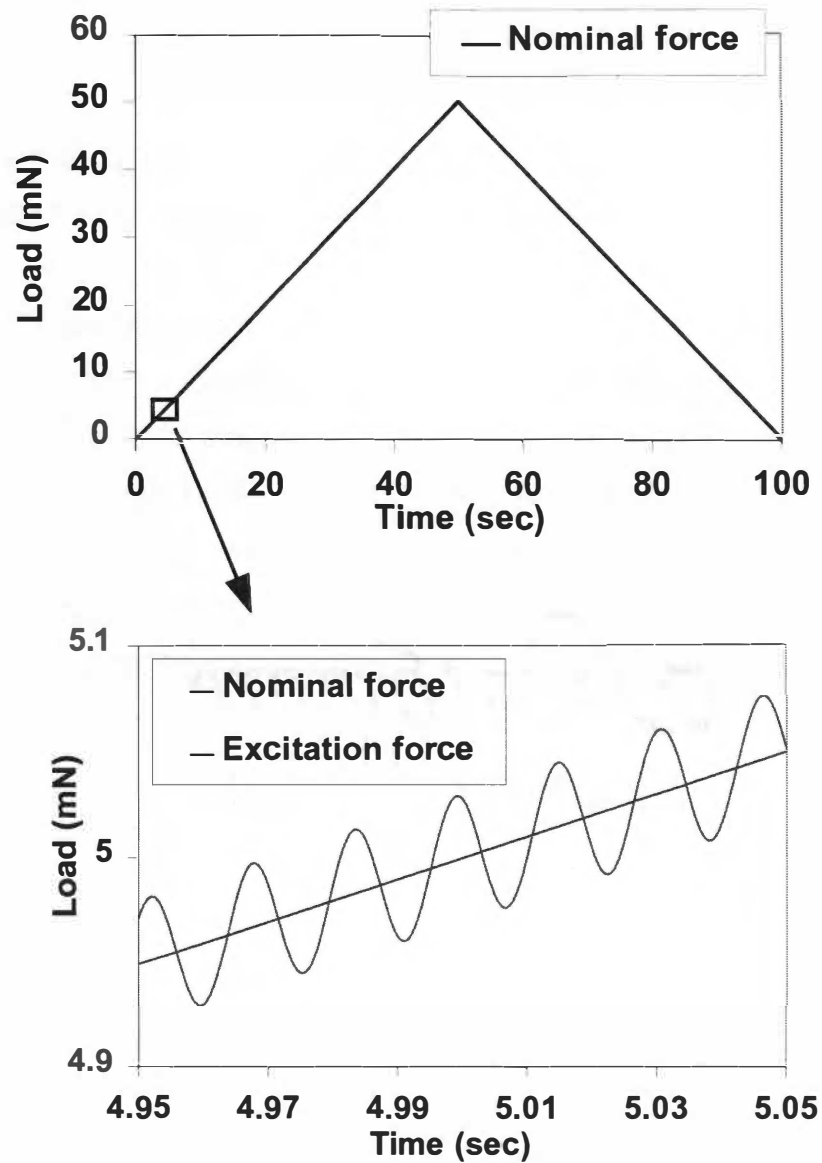


Figure 4. Two plots of indentation load versus displacement showing the small harmonic oscillation applied to the nominal load, for frequency-specific DSI measurements.

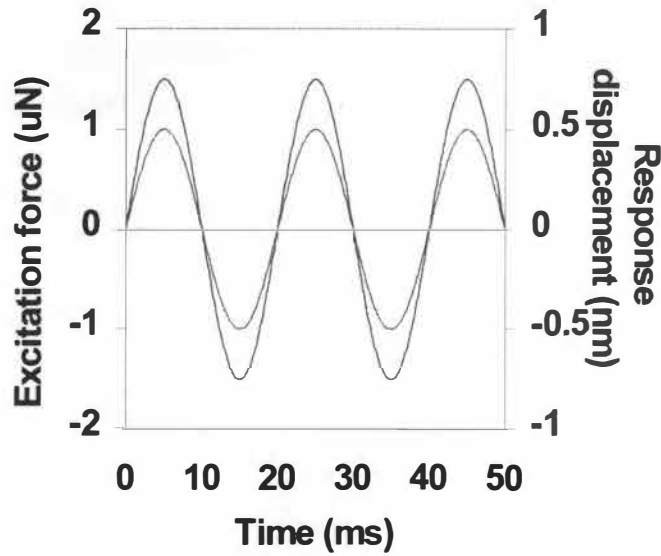


Figure 5. A schematic of the displacement response to an applied excitation force for a purely elastic material. The displacement is in phase with the applied force.

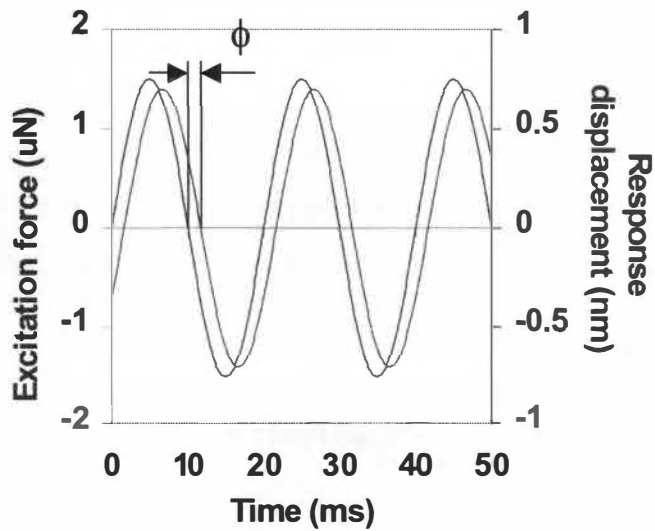


Figure 6. A schematic of the displacement response to an applied excitation force for a viscoelastic material. The displacement lags behind the applied force by a phase angle ϕ .

Using this technique, it has been proposed that the storage modulus, E' , characterizing the elastic behavior of the material, and the loss modulus, E'' , characterizing the internal friction and the damping of the material, can be written as [5, 6]:

$$E' = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (12)$$

and

$$E'' = \frac{\sqrt{\pi}}{2} \frac{C_c \omega}{\sqrt{A}} \quad (13)$$

Moreover, the loss tangent, also known as tangent delta, is defined by:

$$\tan \delta = \frac{E''}{E'} = \frac{C_c \omega}{S} \quad (14)$$

Both static and dynamic mechanical properties can be measured using the frequency-specific DSI. The technique allows one to measure the mechanical properties continuously as the indenter is driven in during loading.

2.2.2. TIME DEPENDENT PLASTICITY

As an indenter is driven into a material, both elastic and plastic deformation processes can occur. According to Tabor [13], when a material is plastically deformed by a Berkovich indenter, the characteristic strain is approximately 8%, and the indentation hardness of the material is approximately

3.3 times its flow stress at this characteristic strain. When an indentation experiment is performed in a creeping material with a constant loading rate, $\dot{P}$, the hardness of the material defined by the equation (1) does not remain constant with penetration depth, as shown in Figure 7. A definition of indentation strain rate has been proposed by Lucas [6, 14]:

$$\dot{\epsilon}_i \equiv \frac{\dot{h}}{h} = \frac{1}{2} \left(\frac{\dot{P}}{P} - \frac{\dot{H}}{H} \right) \quad (15)$$

where $\dot{\epsilon}_i$ is the indentation strain rate, h is the displacement, P is the load, and H is the hardness. This equation suggests that an indentation experiment performed with a pyramidal indenter for which the loading rate is controlled so that the loading rate divided by the load is constant can result in a constant value of the indentation strain rate, if a steady state of the hardness can be reached and $\dot{H} = 0$. Figure 7 includes data that shows that the hardness can indeed remain constant during a constant $\dot{P}/P$ loading. Figure 8 shows that in tests conducted at constant $\dot{P}/P$, the hardness increases systematically with $\dot{P}/P$ (and $\dot{h}/h$). Using the equation (8), it is then possible to measure the stress exponent for creep, n , as shown in Figure 9.

2.2.3. TIME DEPENDENT ELASTICITY

Recently, it has been shown that time dependent elastic properties (viscoelastic) can be measured using DSI. Using this technique, Lucas, Loubet and Oliver [5, 6] measured the dependency of the storage and loss moduli versus frequency for natural rubber, as shown in Figure 10 ($G' = E'/3$ and $G'' = E''/3$, with $\nu = 0.5$ for natural rubber [6]). They also showed that for a Berkovich indenter,

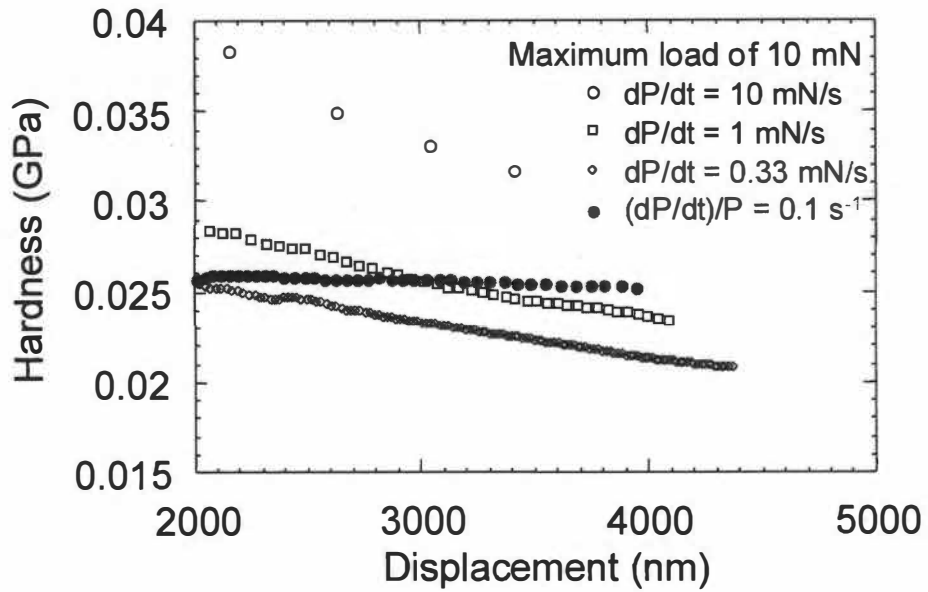


Figure 7. A plot of hardness versus displacement for constant loading rate and constant $\dot{P}/P$ experiments on indium at room temperature [14].

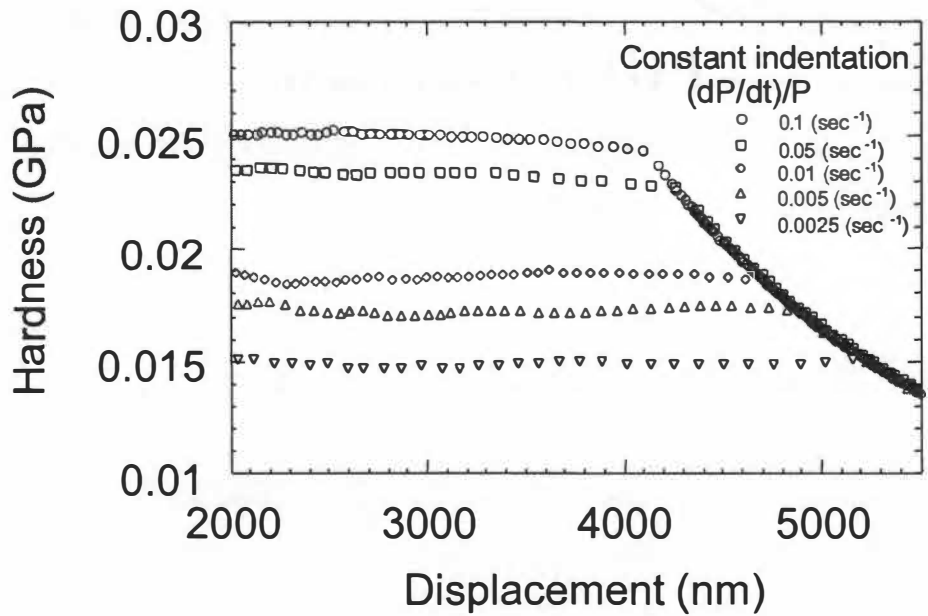


Figure 8. A plot of hardness versus displacement for constant $\dot{P}/P$ experiments on indium at room temperature [14].

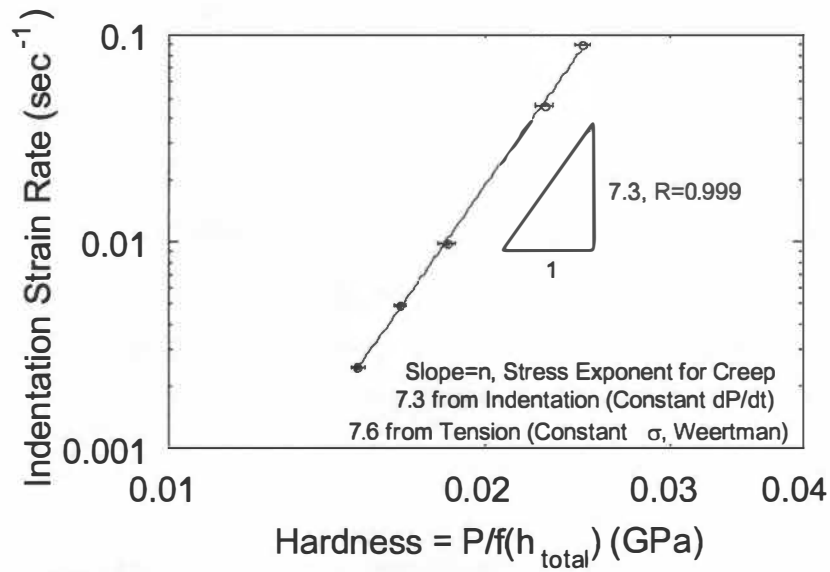


Figure 9. A plot of indentation strain rate versus hardness for data obtained from constant $\dot{P}/P$ for indium at room temperature [14].

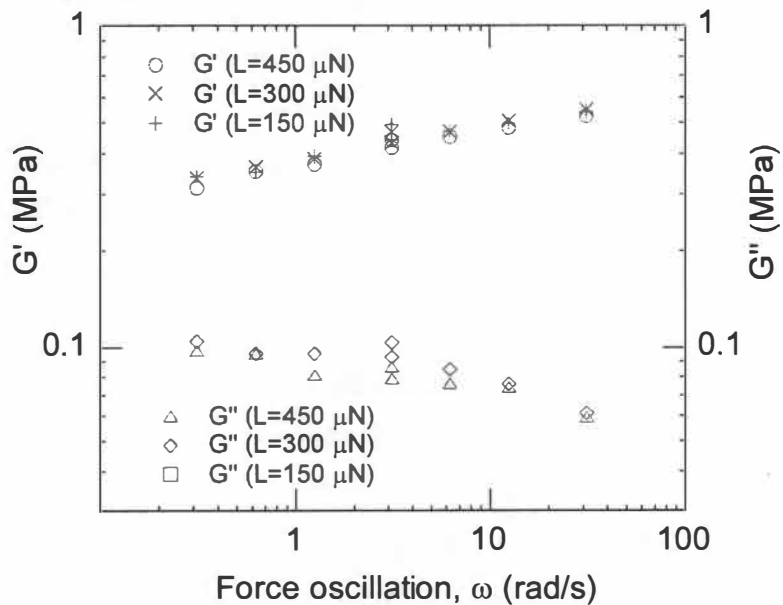


Figure 10. A plot of the shear storage and loss moduli versus angular frequency on a natural rubber at room temperature [5].

the contact stiffness and damping during indentation increase linearly as a function of the penetration, as shown in Figures 11 and 12. Lucas, Oliver and Swindeman [15] subsequently showed how the contact stiffness and damping, and therefore storage and loss moduli, depend on frequency as well.

As previously described, when an indenter is driven into a material, both viscoelastic and plastic deformation processes can occur. Frequency-specific DSI, characterized by small sinusoidal oscillations during the loading process, can thus be used to characterize the viscoelastic behavior.

2.2.4. STRAIN RATE AND FREQUENCY RELATIONSHIP

Figure 13 shows schematically a scale of strain rate and frequency showing their usable range of operation. These two parameters have the same units, since one Hertz is the inverse of one second. We have shown that the strain rate influences the plastic behavior, and therefore the load versus displacement curve from which the hardness is calculated. In a similar manner, the frequency influences the elastic behavior, and therefore the stiffness and damping from which the storage and loss moduli are calculated. This is true if the strain rate and the frequency remain largely separated, and if the amplitude of the oscillations remains small (usually from 1 to 5 nm) compared to indentation depth.

Figure 14 shows a plot of the load versus time for one oscillation during the indentation of polyurethane at a frequency of 64 Hz and a strain rate of 0.05 s^{-1} . The influence of the strain rate on the total signal, characterized by the increase of the static load, is small compared to the size of the oscillation. On the other hand, if the strain rate and the frequency are close together, the increase of the static load dominates the shape of the oscillation cycle (total harmonic load), as shown in Figure 15. Then, the dynamic displacement amplitude and the phase

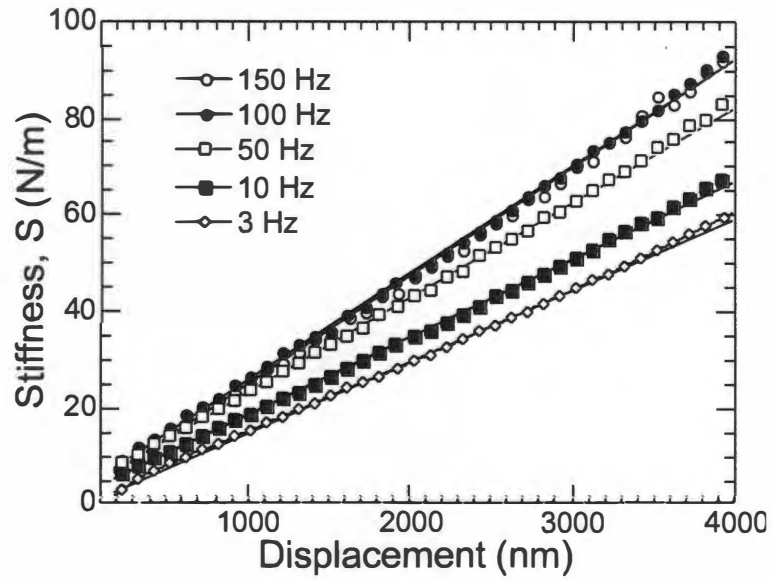


Figure 11. Contact Stiffness versus displacement at various frequencies for tests conducted with a Berkovich indenter on polymeric material [15].

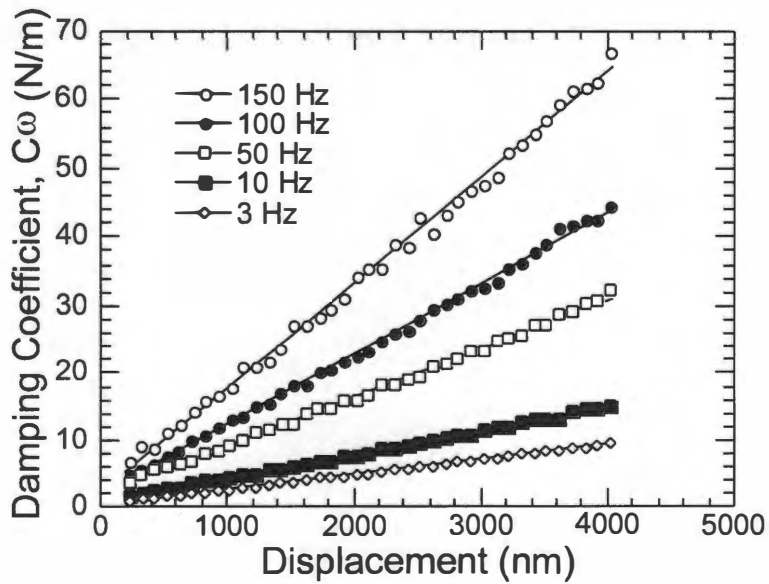


Figure 12. Contact Damping versus displacement at various frequencies for tests conducted with a Berkovich indenter on polymeric material [15].

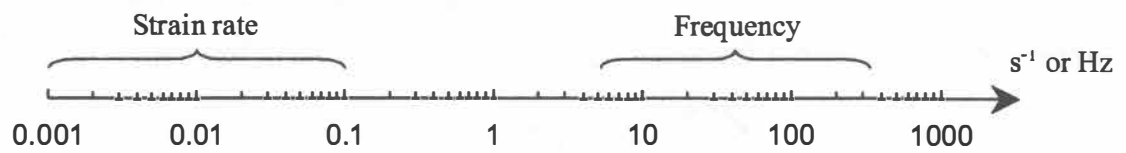


Figure 13. A scale of strain rate and frequency axis showing their usable operating range.

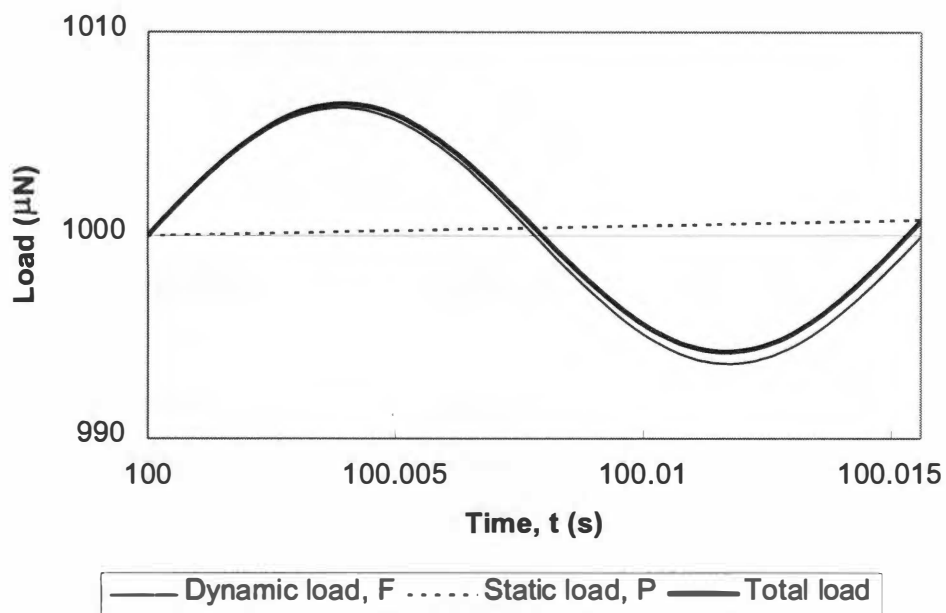


Figure 14. A plot of the load versus time for one oscillation on polyurethane using frequency of 64 Hz and strain rate of 0.05 s^{-1} .

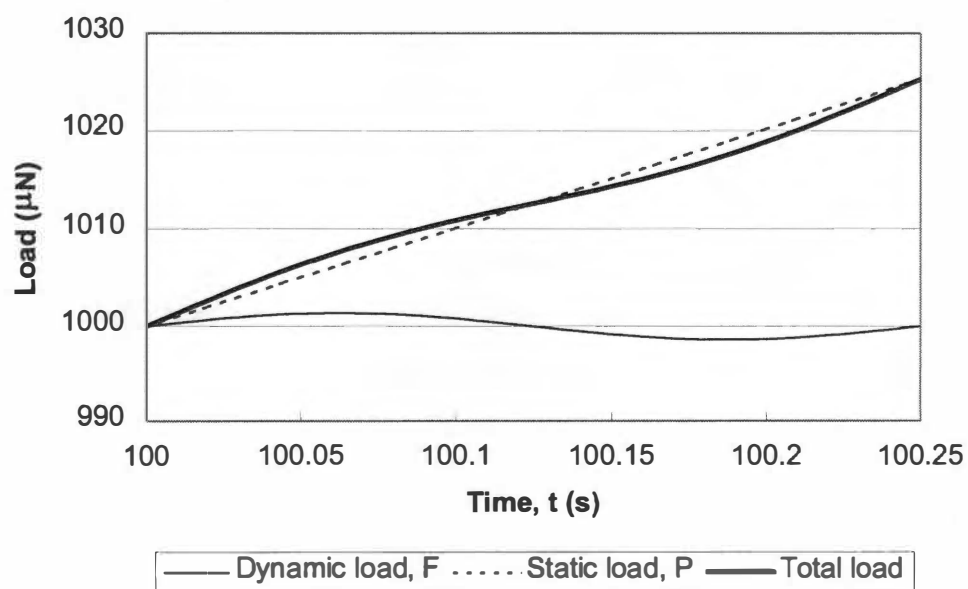


Figure 15. A plot of the load versus time for one oscillation on polyurethane using frequency of 4 Hz and strain rate of 0.1 s^{-1} .

angle cannot be well measured. Therefore, in all the measurements reported here, the usual range of frequency is from 1 to 300 Hz and the usual range of strain rate is from 0.001 to 0.1 s⁻¹.

2.2.5. INDENTATION STRAIN AND STRESS DEFINITIONS

Analyzing the stress and strain applied during an indentation experiment is important to compare results from experiments using various indenter shapes such as the Berkovich pyramid and a cylindrical flat punch.

Indentation using a Berkovich indenter

We have seen previously that according to Tabor [13], for fully developed plastic contact, the characteristic strain for a Berkovich indenter is approximately 8%. When the contact is elastic-plastic, the strain is not uniform around the contact and it is difficult to define an average strain value. Therefore, it is difficult to compare the actual strains and stresses occurring in the material during indentation using a Berkovich indenter with indentation using a flat punch or with DMA.

Indentation using a flat punch indenter

For indentation with a flat punch, we will assume that contact is limited to the end of the punch and there is no contact on the side of the punch. Using this assumption, the characteristic static stress can be defined by:

$$\sigma_s = \frac{P}{A} \quad (16)$$

where σ_s is the static stress, P is the static load, and A is the area of contact. The actual strain generated by the flat punch is very non-uniform with a maximum near the edges and a minimum in the center. In most cases, the contact is elastic. A common definition for the strain relates to the compression of the material between the punch and the substrate, and is defined by:

$$\varepsilon_s = \frac{h}{L_o} \quad (17)$$

where ε_s is the static strain, h is the penetration depth, and L_o is the initial thickness of the material.

Frequency-specific DSI allows the measurement of the dynamic properties. By analogy with DMA, the characteristic dynamic stress, using frequency-specific DSI techniques and a flat punch indenter, can be defined by:

$$\sigma_d = \frac{F_o}{A} \quad (18)$$

where σ_d is the dynamic stress, and A is the area of contact. The resulting dynamic strain can then be defined by:

$$\varepsilon_d = \frac{z_o}{L_o} \quad (19)$$

where ε_d is the dynamic strain, and L_o is the initial thickness of the material.

2.3 DYNAMIC MECHANICAL ANALYSIS (DMA)

The first attempt to do oscillatory experiments to measure the elasticity of a material was by Poynting [17] in 1909. Commercial instruments first appeared in the 1950's, including the Weissenberg Rheogoniometer and the Rheovibron. By the time Ferry wrote his classic textbook on the *Viscoelastic Properties of Polymers* [7] in 1961, dynamic measurements were an integral part of polymer science. Ferry gives an excellent development of the theory. In 1967, McCrum et al. [8] collected all available information on DMA and DEA (dielectric analysis) in their landmark textbook. Commercial instruments became more user-friendly following the revolution in computer technology.

DMA is conducted by applying an oscillating force to a sample and analyzing the material's response to that force. The sample is usually loaded by a constant load. By imposing a sinusoidal oscillation of alternating stress, the sample will deform sinusoidally. For linear viscoelastic behavior, the stress and strain will both vary sinusoidally, but the strain lags behind the stress. The dynamic applied stress can be written

$$\sigma = \sigma_o \sin \omega t \quad (20)$$

where σ is the dynamic stress at time t , σ_o is the amplitude of the dynamic stress, and ω is the angular frequency. The resulting dynamic strain, which will depend upon the viscoelastic behavior, can be written as

$$\varepsilon = \varepsilon_o \sin(\omega t + \delta) \quad (21)$$

where ε is the dynamic strain at time t , ε_0 is the amplitude of the dynamic strain, and δ is the phase lag.

From these measurements, the storage or elastic modulus, E' , related to the amount of energy the material gives back after having been deformed, can be calculated from [7]:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta = \frac{f_0}{bk} \cos \delta \quad (22)$$

where b is a constant that depends on the geometry of the DMA sample, f_0 is the dynamic force applied at the peak of the sine wave, and k is the dynamic sample displacement at its peak value. The amount of energy lost to friction and internal motions is related to the loss modulus, E'' . It is calculated from [7]:

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta = \frac{f_0}{bk} \sin \delta \quad (23)$$

The tangent of the phase angle is a basic material property at a given frequency and temperature. Many early instruments recorded only the phase angle, and consequently the early literature uses the loss tangent as the basic measured material property. The loss tangent is an indicator of how efficiently the material loses energy to molecular rearrangements and internal friction. It is also the ratio of the loss to the storage moduli, and is, therefore, independent of the contact area. It is defined as

$$\tan \delta = \frac{E''}{E'} \quad (24)$$

For DMA, static and dynamic stress and strain can be defined in a manner very similar to indentation with a flat punch. The characteristic static stress is defined by:

$$\sigma_s = \frac{P}{A} \quad (25)$$

where σ_s is the static stress, P is the static load, and A is the area of contact. The resulting engineering static strain is then defined by:

$$\varepsilon_s = \frac{\Delta L}{L_o} \quad (26)$$

where ε_s is the static strain, ΔL is the elongation ($\Delta L = L - L_o$), and L_o is the initial length of the material. The characteristic dynamic stress is defined by

$$\sigma_d = \frac{f_o}{A} \quad (27)$$

where σ_d is the dynamic stress, f_o is the dynamic force applied at the peak of the sine wave, and A is the area of contact. The resulting dynamic strain is then defined by:

$$\varepsilon_d = \frac{k}{L_o} \quad (28)$$

where ε_d is the dynamic strain, k is the dynamic sample displacement at its peak value, and L_o is the initial length of the material.

CHAPTER 3 EXPERIMENTAL EQUIPMENT

3.1 INDENTATION

3.1.1 THE NANO INDENTER[®] DCM

All indentation tests were performed using a Nano Indenter[®] DCM [15], (MTS Nano Instruments Innovation Center, Oak Ridge, TN). Figure 16 is a schematic of the instrument. The indenter is supported inside the indentation head by two leaf springs designed to limit the motion of the indenter column to the vertical direction only. The load on the indenter is generated by an electromagnetic coil and a permanent magnet. The resolution of the loading system is 1 nN. The displacement of the indenter column is measured with a parallel plate capacitive displacement gauge with a manufacturer's specified resolution of 0.0002 nm. The system was controlled and data acquired with the MTS TestWorks software on a personal computer.

3.1.2 CONTINUOUS STIFFNESS MEASUREMENT (CSM)

Continuous Stiffness Measurement (CSM) [1, 4] (also called frequency-specific DSI) is an option of the Nano Indenter[®] DCM. This option allows one to measure the elastic contact stiffness continuously as the indenter is loaded into the sample. This is accomplished by adding a small harmonic force at a specific excitation frequency to the nominal force on the indenter.

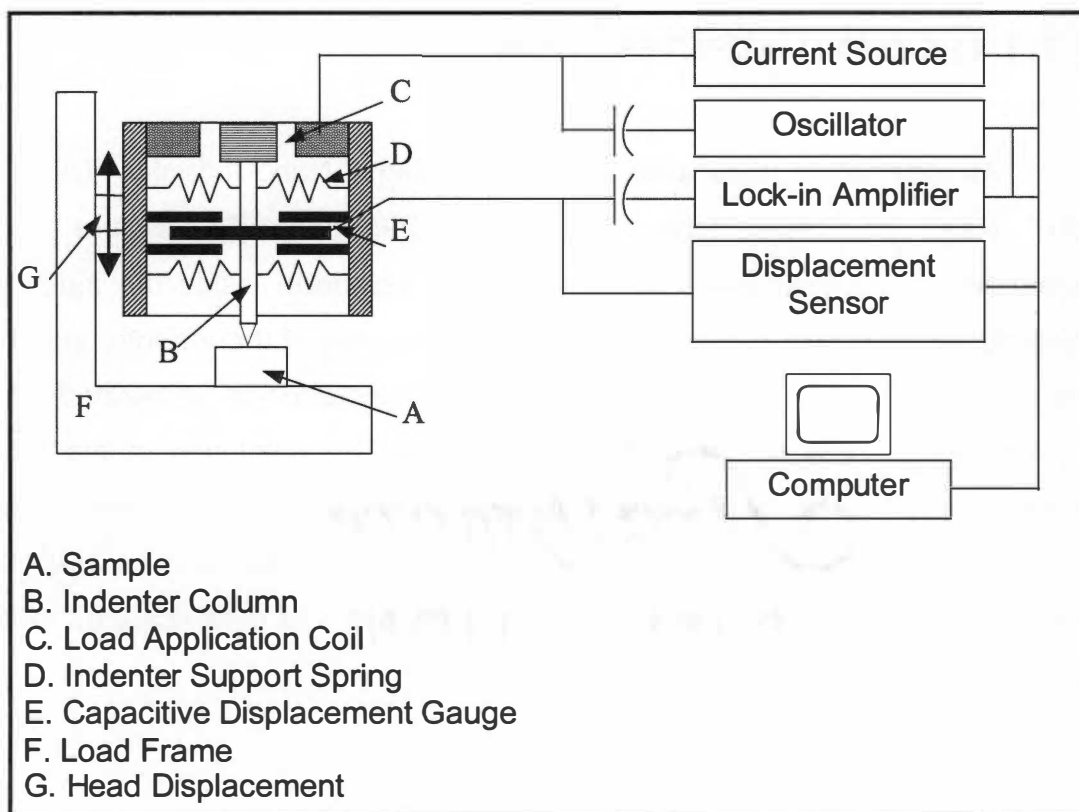


Figure 16. A schematic of the Nano Indenter® DCM.

Dynamic Models

The two measurements performed during an experiment, the displacement amplitude and the phase angle between the force excitation and the displacement response, are a composite of the response of the instrument and the material being indented. In order to obtain the properties of the material, the instrument characteristics must be properly calibrated and removed from the data. A schematic of the components of the Nano Indenter[®] DCM assembly necessary for consideration in a dynamic model is shown in Figure 17-a. A spring-dashpot model for the components is presented in Figure 17-b. All motion is restricted to one dimension so that the system (indenter in contact with the material) is well modeled by a simple harmonic oscillator, as shown in Figure 17-c. An analysis of this model yields the ordinary differential equation

$$m\ddot{z} + C\dot{z} + Kz = F(t) \quad (30)$$

where K and C are respectively the equivalent (or measured) stiffness and damping, and m is the mass of the indenter. For a forcing function of the form

$$F(t) = F_0 e^{i\omega t} \quad (31)$$

the particular displacement solution is assumed to be of the form

$$z(t) = z_0 e^{i(\omega t - \phi)} \quad (32)$$

In other words, the displacement oscillates at the same frequency as the force (ω), but lags by a phase angle, ϕ . Substituting the particular solution (32) into equation (30) and equating magnitudes yields

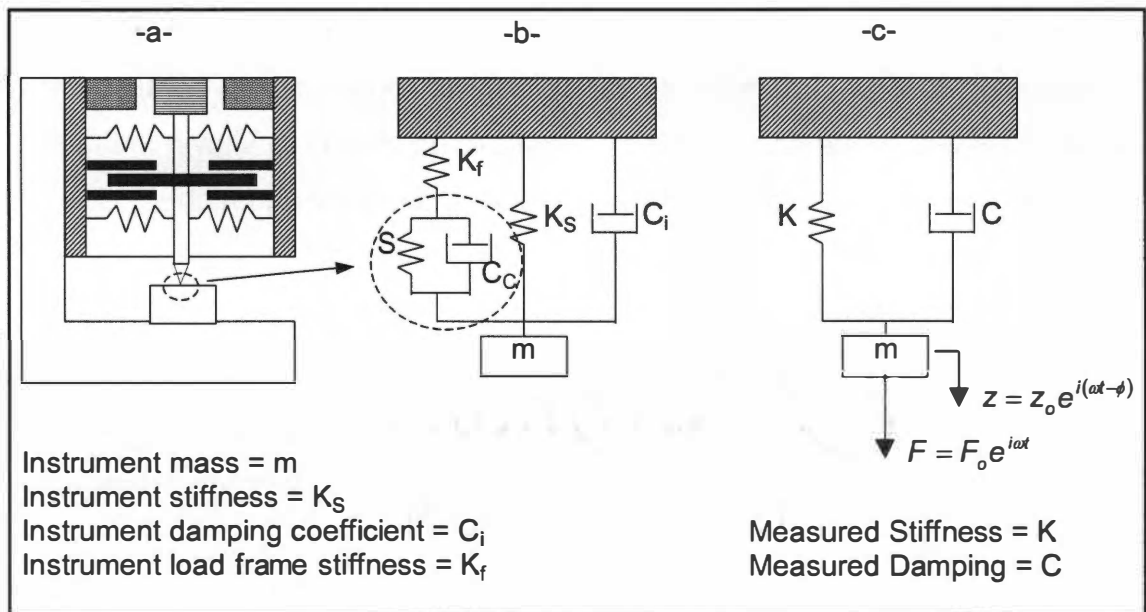


Figure 17. Dynamic models of the Nano Indenter® DCM. a-Schematic of the instrument. b-Instrument model. c-Equivalent model.

$$\left| \frac{F_o}{z_o} \right| = \sqrt{(K - m\omega^2)^2 + (C\omega)^2} \quad (33)$$

and

$$\tan \phi = \frac{C\omega}{K - m\omega^2} \quad (34)$$

These two equations can be solved simultaneously for K and C giving

$$K = \frac{F_o}{z_o} \cos \phi + m\omega^2 \quad (35)$$

and

$$C\omega = \frac{F_o}{z_o} \sin \phi \quad (36)$$

An analysis of the relationship between the instrument model and the equivalent model yields the following equations

$$K = \left(\frac{1}{S} + \frac{1}{K_f} \right)^{-1} + K_s \quad (37)$$

where S is the contact stiffness of the material, K_f is the load frame stiffness, K_s is the stiffness of the support springs, and

$$C = C_c + C_f \quad (38)$$

where C_c is the contact damping (damping in the specimen), and C_i is the damping of the instrument.

Finally, by substituting respectively the equations (35) and (36) into equations (37) and (38), the stiffness and damping of the contact are given by

$$S = \left[\frac{1}{\frac{F_o}{z_o} \cos \phi - (K_s - m\omega^2)} - \frac{1}{K_f} \right]^{-1} \quad (39)$$

and

$$C_c \omega = \frac{F_o}{z_o} \sin \phi - C_i \omega \quad (40)$$

During an experiment, the excitation angular frequency, ω , is fixed, and the excitation and displacement amplitudes (F_o and z_o), and the phase angle (ϕ) are measured. Thus, by knowing K_f , K_s , m and C_i , and using the equations (39) and (40), it is possible to calculate the stiffness and the damping of the contact. Therefore, calibrations are necessary to precisely determine the load frame stiffness, K_f , the stiffness of the support springs, K_s , the mass of the indenter, m , and the damping of the instrument, C_i .

Instrument Calibrations

The scope of this discussion will be limited to the calibrations of K_s , m and C_i . All these parameters are determined by analyzing the quasi-static or dynamic response of the system when the indenter is hanging free (no contact between indenter and surface).

The first step is the instrument stiffness calibration. This is done quasi-statically and as a function of the indenter displacement. Over all the displacement range, a constant loading rate is applied to the indenter during which the displacement is measured. The quasi-static stiffness of the instrument is then calculated using the equation

$$S = \frac{\Delta P}{\Delta h} \quad (41)$$

An example of the instrument stiffness calibration is shown in Figure 18.

The second step is the instrument mass calibration. The dynamic compliance (excitation response divided by the excitation force) is measured as a function of the frequency. An example of this measurement is shown in Figure 19. Then the resulting data are fitted to the theoretical equation:

$$\left| \frac{z_o}{F_o} \right| = \frac{1}{\sqrt{(K - m\omega^2)^2 + (C\omega)^2}} \quad (42)$$

This fit provides the value of the mass of the indenter.

The last step is the damping calibration, which is done at the resonance frequency of the instrument. Over all the displacement range, a constant loading rate and a constant oscillation force are applied to the indenter, during which the harmonic displacement response and phase angle are measured. The dynamic damping of the instrument is then calculated using the equation

$$C_i \omega = \frac{F_o}{z_o} \sin \phi \quad (43)$$

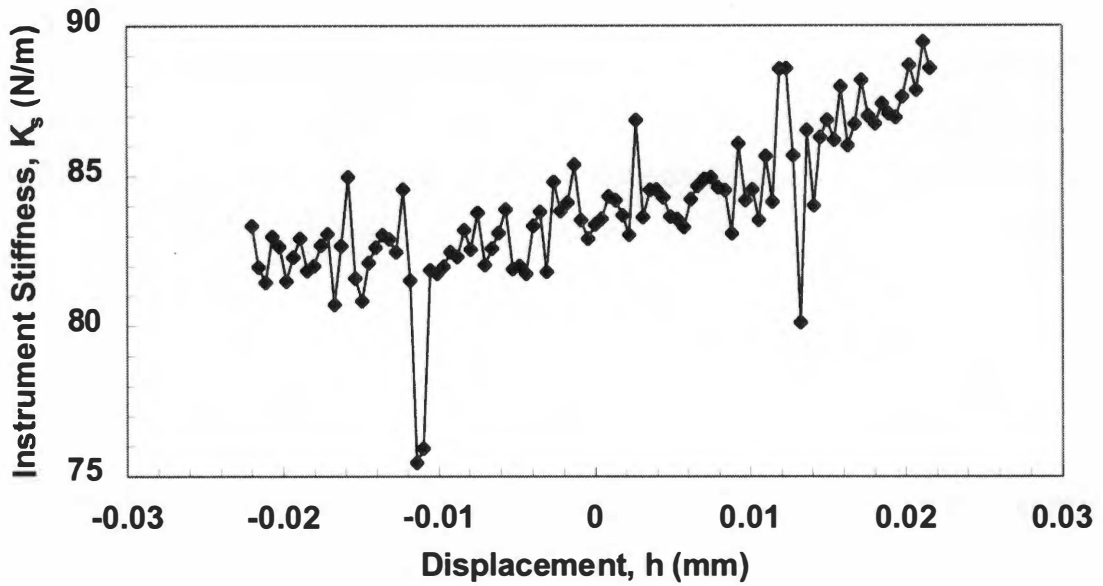


Figure 18. A plot of stiffness versus displacement, showing the instrument stiffness calibration.

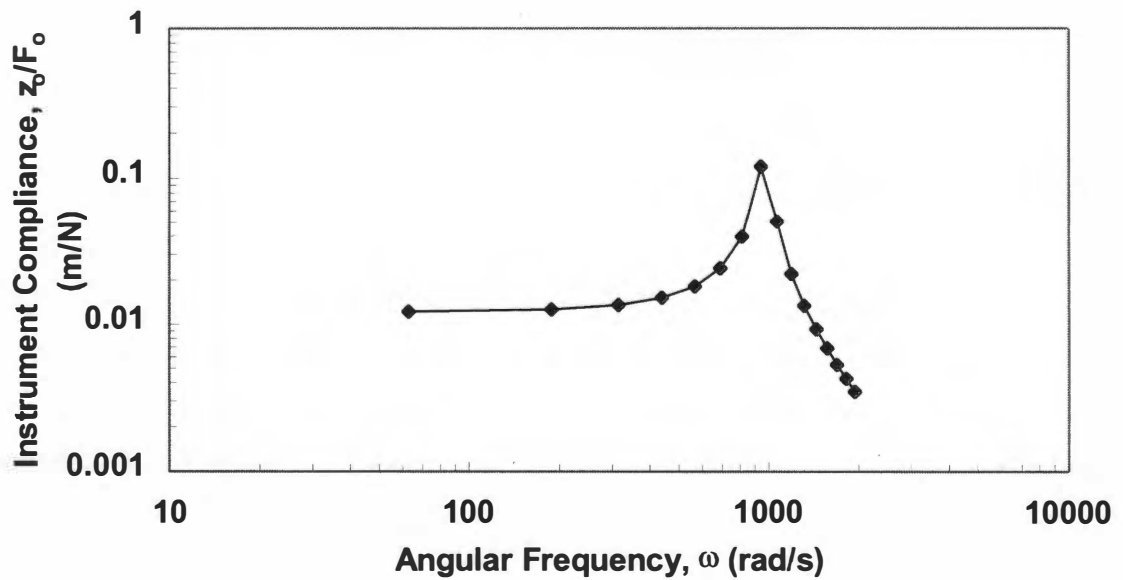


Figure 19. A plot of compliance versus displacement used for the instrument mass calibration.

An example of the instrument damping calibration is shown in Figure 20.

3.1.3 DESCRIPTION OF THE INDENTATION TIPS

Two different tips were used for the indentation testing: a Berkovich triangular pyramid and a flat circular punch.

Berkovich

The Berkovich tip is a three-sided pyramid with a centerline-to-face angle of 65.3° , as shown in Figure 21. It is manufactured from diamond for its high resistance to elastic and plastic deformation and abrasion. The Berkovich indenter generates a variable area of contact, that scales as the square of the depth of penetration.

Flat punch

The flat punch tip is a cylindrical punch with a diameter of $89\ \mu\text{m}$, as shown in Figure 21. It is manufactured from a glass fiber. The flat punch indenter generates a constant area of contact once it is in full contact with the material.

3.2 DMA

All Dynamic Mechanical Analysis (DMA) tests were performed using a DMTA VTM (Rheometric ScientificTM, Piscataway, NJ). This instrument gives, among other things, the viscoelastic properties of polymeric materials as a function of frequency. Measurements of storage and loss moduli, and loss tangent using tension and compression tests were of greatest interest in this study.

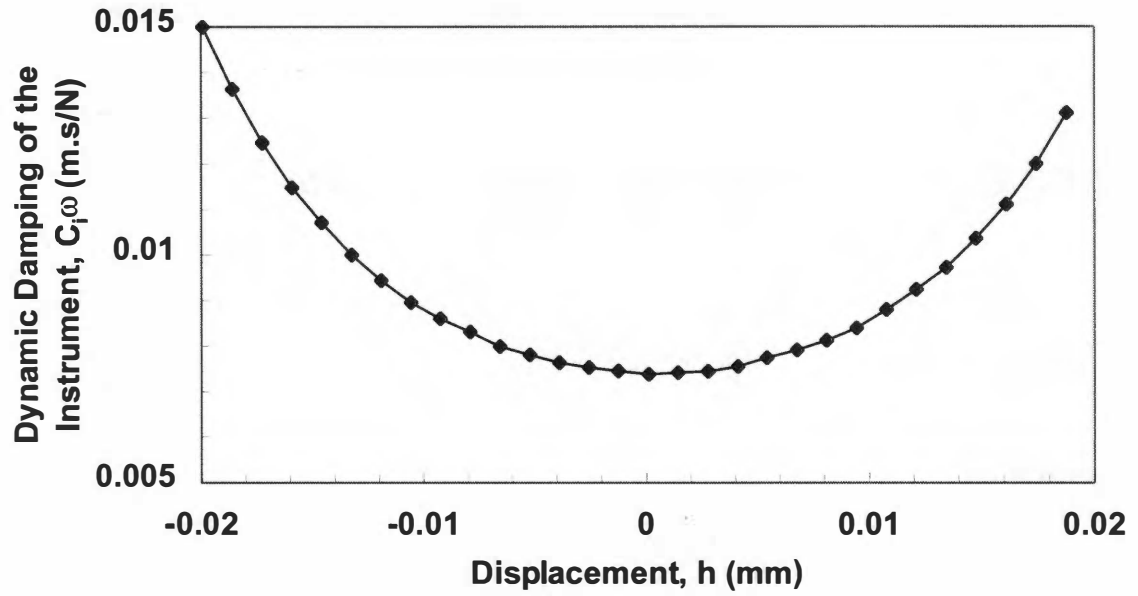


Figure 20. A plot of dynamic damping versus displacement, showing the dynamic damping of the instrument used for the calibration.

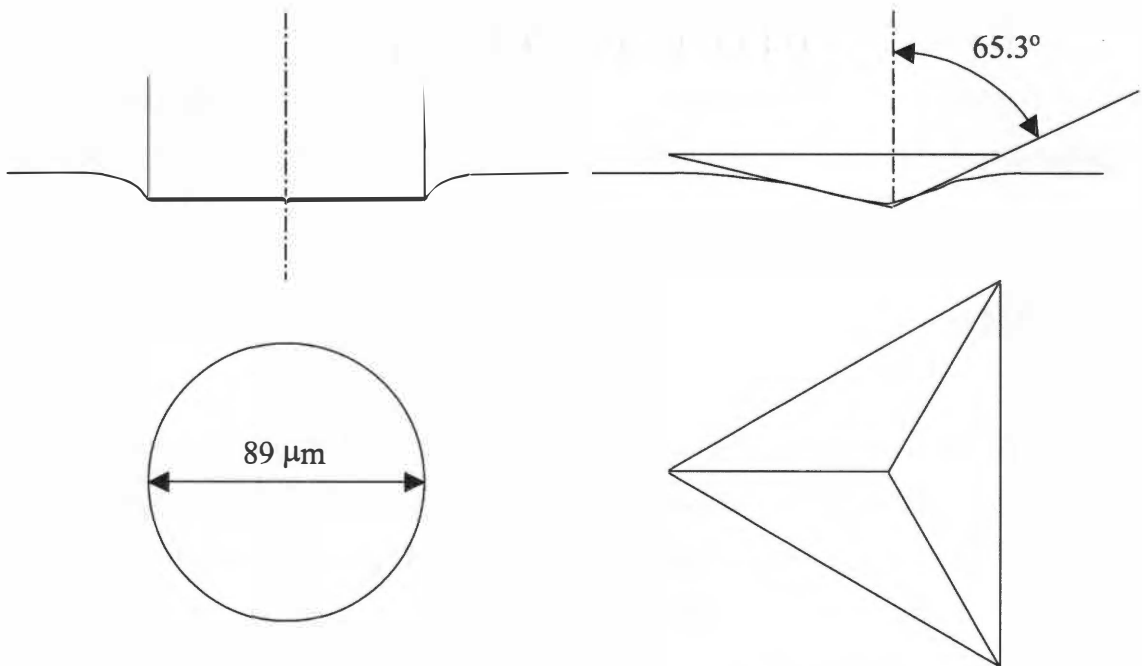


Figure 21. Schematic of the flat circular punch and Berkovich indenters.

Figure 22 is a schematic of the instrument. The drive shaft is driven by supplying a current to the servomotor. The motion of the drive shaft is detected by a position sensor consisting of a static probe and a target attached to the drive shaft. Two disk-shaped springs support the servomotor and drive shaft assembly. The resolution of the applied force is 1 mN, and the resolution of the drive shaft displacement is less than 1 nm. The frequency range specified is 10^{-6} to 200 Hz. The operation of the system and the acquisition of data are controlled through the RSI software package "Orchestrator".

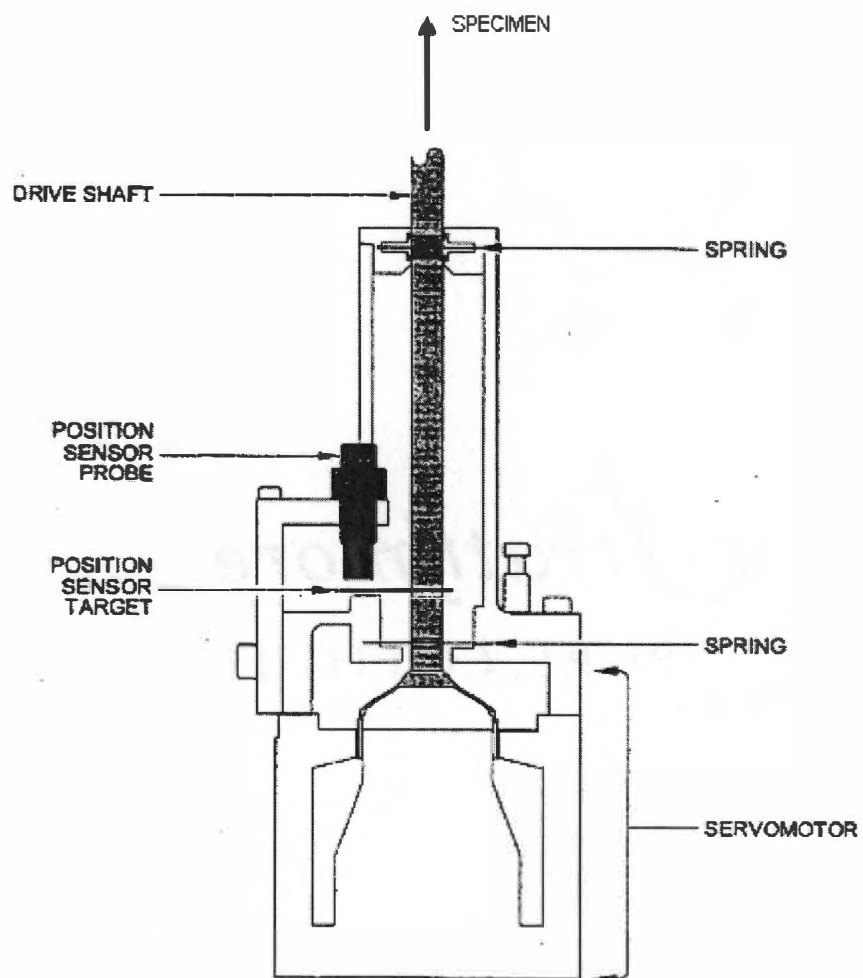


Figure 22. A schematic of the DMTA V Drive assembly.

CHAPTER 4 EXPERIMENTAL TECHNIQUES AND DETAILS

4.1 IMPROVEMENTS FOR POLYMER AND ELASTOMER TESTING AT VARIOUS FREQUENCIES

In order to measure the viscoelastic properties at various frequencies using nanoindentation techniques, two major instrument improvements were developed: (1) phase angle correction and (2) dynamic calibration of the stiffness and damping of the instrument. Moreover, minor improvements were also made to the test procedure, such as the detection of the first point of contact, and the time constant.

4.1.1 PHASE ANGLE CORRECTION

The viscoelastic properties, E' and E'' , defined by the equations (12) and (13), are dependent upon the dynamic stiffness and damping of the contact, S and C_c . Equations (39) and (40) show that these dynamic calculations can be significantly affected by the phase angle measurement, ϕ . Therefore, a precise measure of the phase angle is needed in order to determine the viscoelastic properties as a function of the frequency. A new technique was developed in order to improve the precision of the phase angle measurement over the entire range of frequency of the instrument.

A brief description of the electrical connections in the instrument, presented in Figure 23, is needed to understand the discussion that follows. The

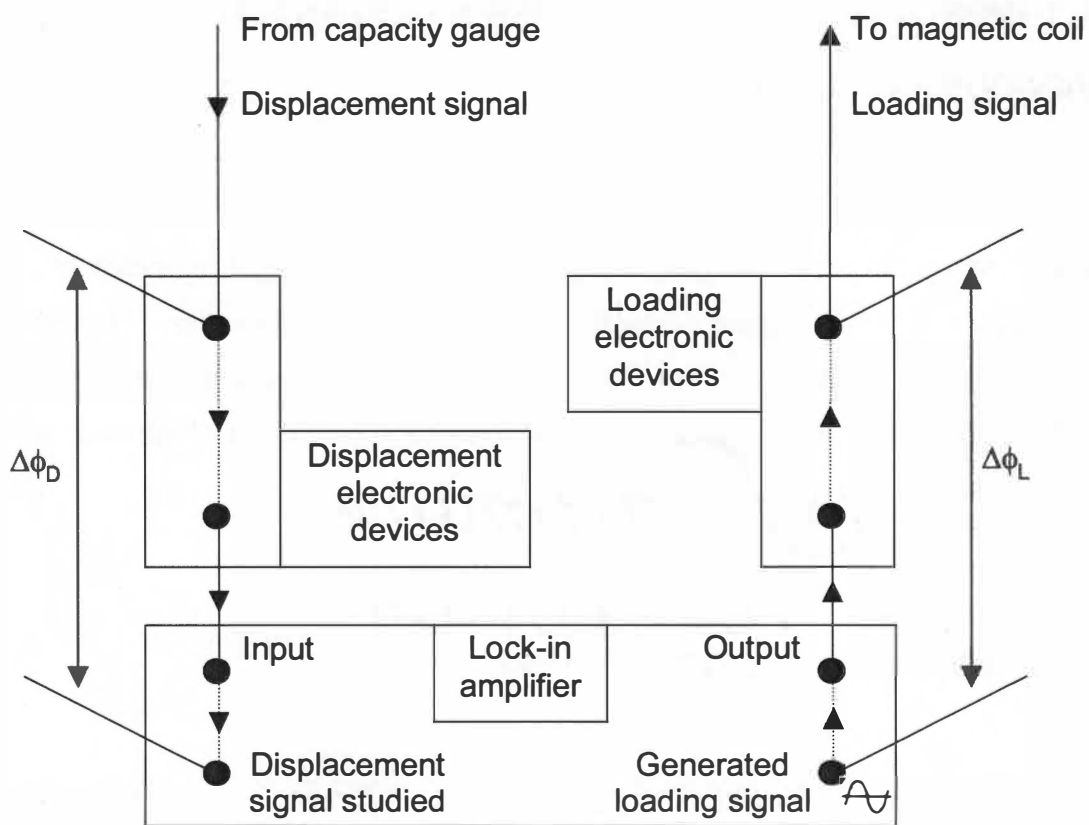


Figure 23. A schematic of the Nano Indenter® electrical connections.

indenter column is driven by a current induced in the magnetic coil. This current, called the loading signal, is generated by a lock-in amplifier and is sent to the coil via electronic devices. The displacement of the column is measured by a capacitive displacement gauge generating a signal called the displacement signal. This signal passes through electronic devices before being analyzed by the lock-in amplifier. The phase angle is the phase difference between the displacement and the load signals analyzed in the lock-in amplifier. The lock-in amplifier has the ability to offset the phase angle to any desired value.

The normal technique used by the Nano Indenter[®] DCM to correct the phase angle is called “zero the phase.” This technique involves comparing the loading signal after it has passed through all of the electronics to the coil to the generated one. The phase angle measured between these two signals is then subtracted from the generated signal by the offset function. After several modifications of the program that executes the “zero the phase” procedure (language C++), this function was found to be capable of working at various frequencies with an improvement in accuracy. Using these modifications, measurements were made of the dynamic compliance and the phase angle after performing “zero the phase” at each frequency while the indenter was hanging free. The result of the dynamic compliance was not significantly changed compared to the compliance measurement performed during the mass calibration shown in Figure 19. This confirmed that the dynamic compliance measurement is independent of the “zero the phase” procedure. The phase angle results presented in Figure 24 show an expected frequency dependence with a rise to 90° at the resonance frequency (156 Hz). Nevertheless, the phase angle rises above 180° at frequency above resonance, which should not happen according to the instrument model. The theoretical phase angle versus frequency determined from a dynamic compliance fit (presented below) is also shown in Figure 24. Comparison of the two phase angles shows that a phase shift is added to the measurement. The “zero the phase” procedure eliminates the

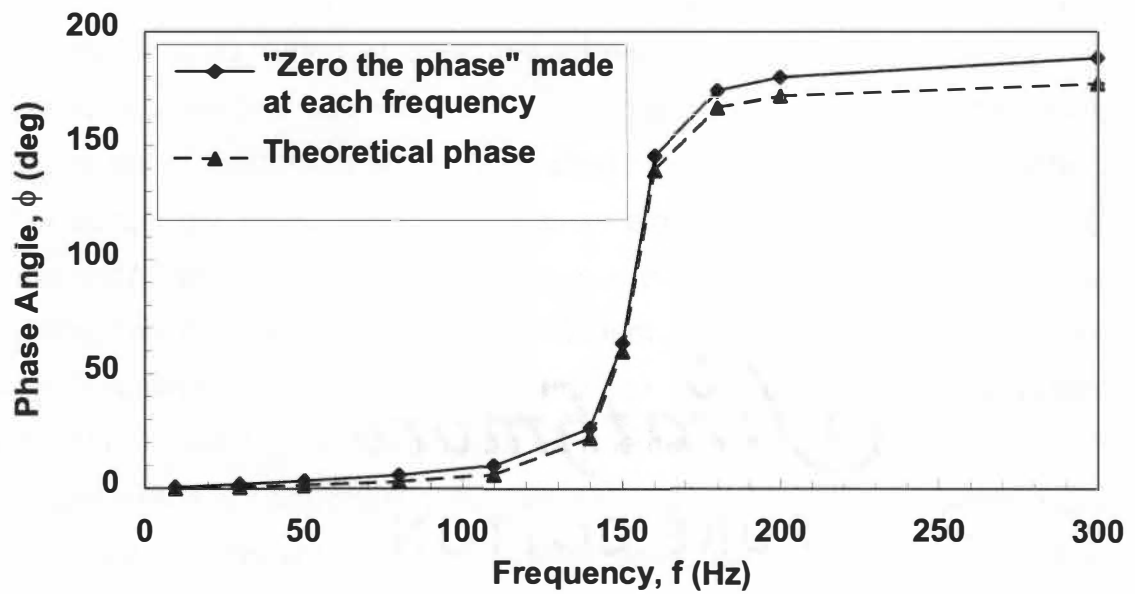


Figure 24. Comparison of the phase angle after zeroing the phase at each frequency with the theoretical phase angle according to the compliance fit versus frequency. The indenter is free-hanging.

phase shift, $\Delta\phi_L$, in the loading signal induced by the filters in the electronic devices and the lock-in amplifier (as shown in Figure 23), but it does not eliminate the phase shift, $\Delta\phi_D$, in the displacement signal due to the filters in the electronic devices and the lock-in amplifier.

A new approach was developed to correct the phase angle over the entire range of frequency. The first step of the phase angle correction is to measure the dynamic compliance and the phase angle of the instrument as a function of frequency while the indenter is hanging free in the middle of the displacement range, $h=0$. The offset function was set to zero. Then, the dynamic compliance is fitted to the theoretical equation (42). The dynamic compliance measurement and its fit versus frequency are shown in Figure 25. This fit gives the dynamic stiffness and damping, K_s and C_i , and the mass, m , of the instrument. Using these three parameters and equation (34), one can then determine the frequency dependence of the theoretical phase angle. This theoretical value is the phase angle the instrument should have to give the frequency dependence of the measured compliance. The phase angle measurement and the theoretical phase according to the compliance fit versus frequency are shown in Figure 26. The measured phase angle falls below zero degrees at low frequency and rises above 180° above the resonance frequency (156 Hz), which shows that a phase shift is needed. The difference between these two phases is the phase shift induced by the different filters in the electronic devices and the lock-in amplifier. This difference represents a phase correction that needs to be applied to the phase angle measurement. In order to set the phase angle correction using the offset function, the phase angle correction versus frequency was fitted to the equation

$$\text{Phase correction} = m_1 \times f^{m_4} + m_2 + \frac{m_3}{f^{m_5}} \quad (44)$$

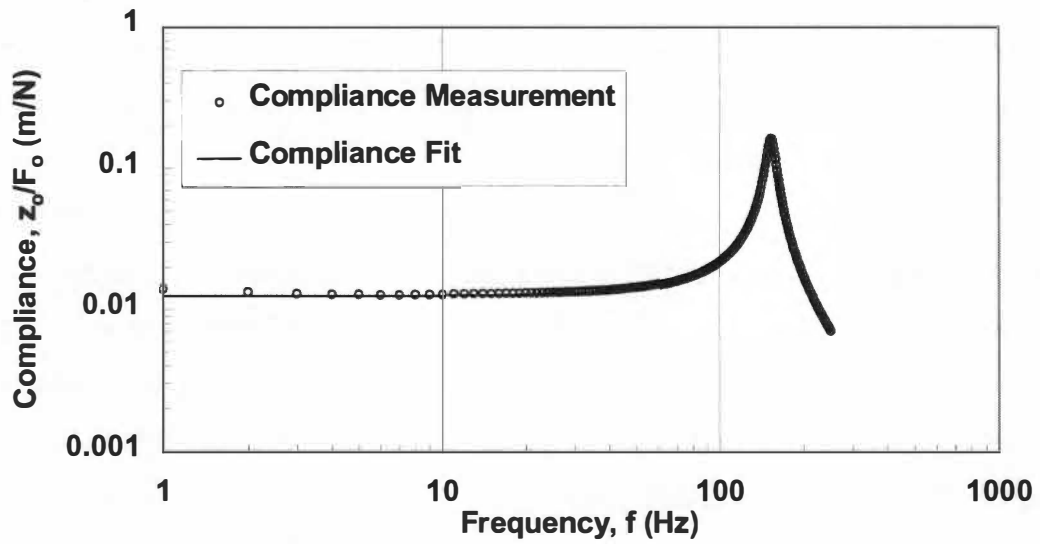


Figure 25. A plot of dynamic compliance measurement and its fit versus frequency. The indenter is free-hanging.

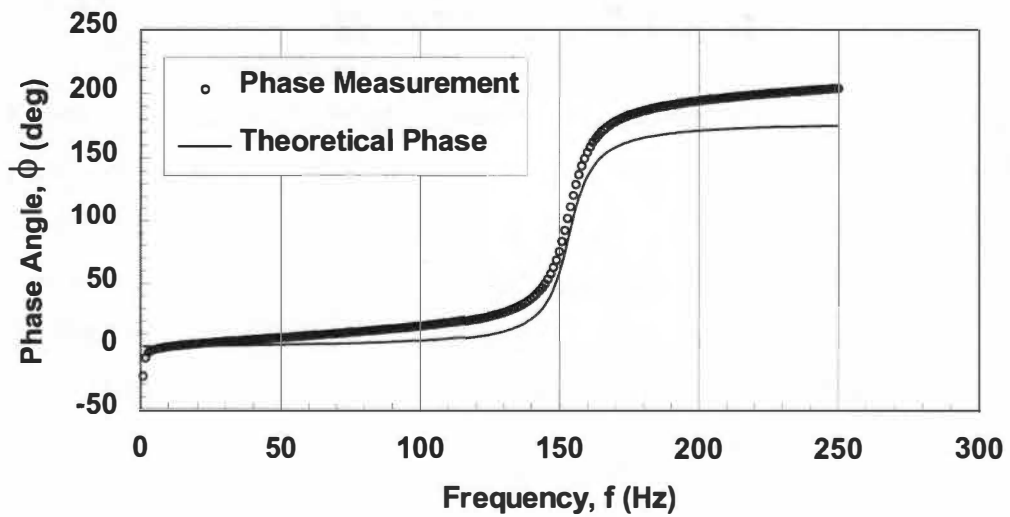


Figure 26. A plot of the measured phase angle and the theoretical phase angle according to the model for the dynamic compliance versus frequency.

where m_1 through m_5 are fitting constants and f is the frequency. The frequency dependence of the phase angle correction and its fit are shown in Figure 27.

4.1.2 DYNAMIC STIFFNESS AND DAMPING CALIBRATION OF THE INSTRUMENT

It is also necessary to accurately and precisely determine the dynamic stiffness and damping of the instrument as a function of the indenter position in the head in order to use these calibrations in the calculation of the stiffness and damping of the contact.

As discussed in section 3.1.2, the usual stiffness calibration of the instrument's springs, K_s , is done quasi-statically as a function of the displacement of the indenter, h . K_s is important because it is used in equation (39) in order to determine the contact stiffness, S . When the measurement of the contact stiffness is done dynamically, as in all of this work, the dynamic stiffness of the instrument's springs must be used in this equation instead of the quasi-static stiffness.

A new experimental method was written to provide measurements of the dynamic stiffness and damping of the instrument. The equations used for these dynamic measurements are

$$K_s = \frac{F_o}{z_o} \cos \phi + m\omega^2 \quad (45)$$

and

$$C_i\omega = \frac{F_o}{z_o} \sin \phi \quad (46)$$

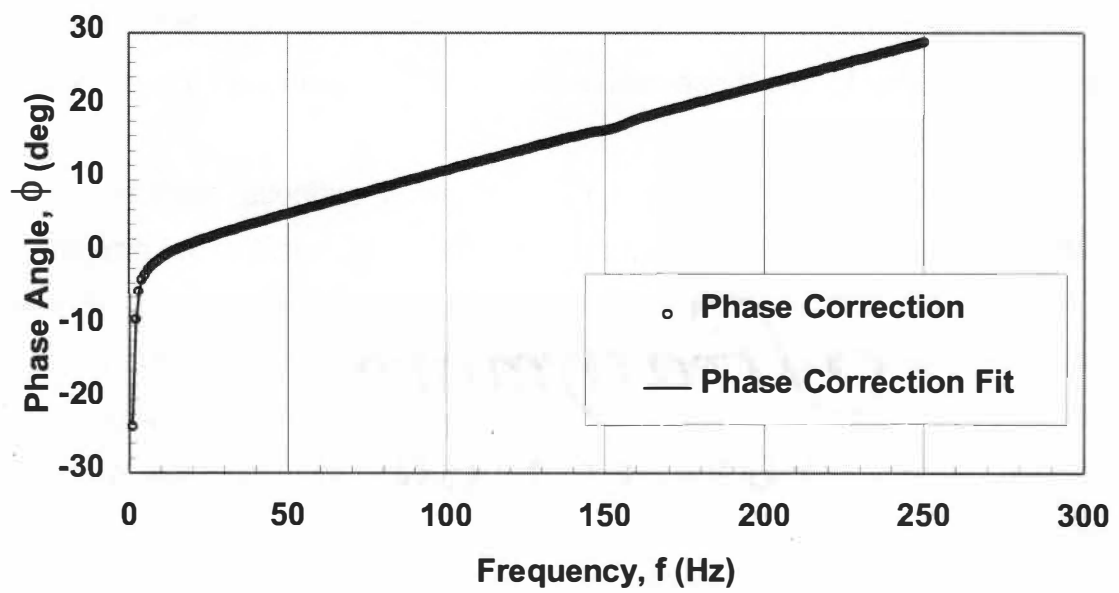


Figure 27. A plot of phase angle correction and its fit versus frequency.

In the new experimental method, the indenter traverses the entire displacement range and records along the way the dynamic stiffness and damping of the instrument at a specific frequency.

Figures 28 and 29 show, respectively, the dynamic stiffness and damping of the instrument versus displacement of the indenter at frequencies from 30 to 200 Hz at every 5 Hz. Although there are small differences between results at each frequency the differences are not large enough to be taken into account in data analysis procedures. Thus, the dynamic stiffness and damping of the instrument were calibrated at only one frequency (75 Hz) by fitting the dynamic measurements to a polynomial equation (fifth raw).

4.2 INDENTATION TESTS

The indentation tests were performed using a Nano Indenter[®] DCM at room temperature (24°C). Two different tips were used for the tests: a Berkovich triangular pyramid and a circular flat punch. A polyurethane (PU) and a polydimethylsiloxane (PDMS) sample were tested with both tips at various frequencies using the Continuous Stiffness Measurement. The harmonic force was controlled such that the resulting displacement oscillation was maintained at 5 nm.

4.2.1 TIP GEOMETRY

For large indentations using a perfect Berkovich tip, the area of contact is a function of the contact depth, h_c , and can be written as:

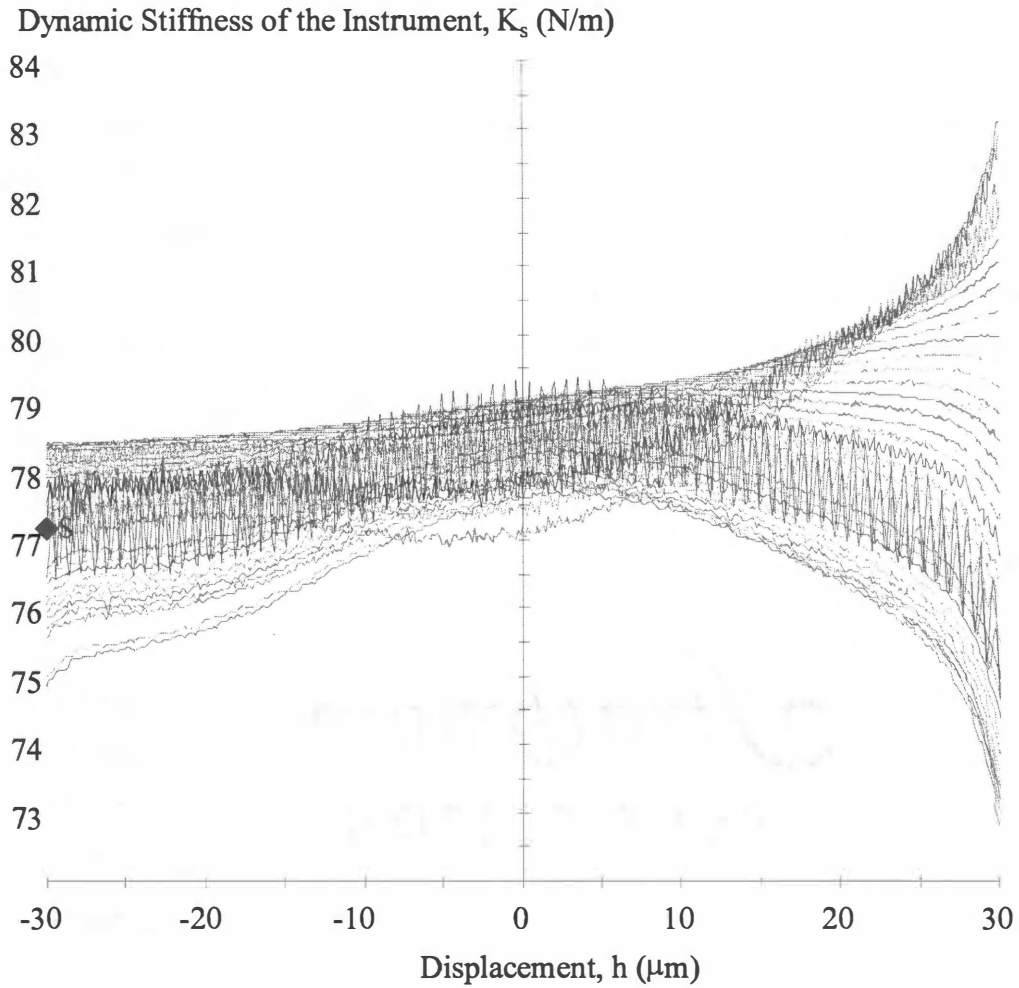


Figure 28. Dynamic stiffness of the instrument versus displacement of the indenter at various frequencies (from 30 to 200 Hz every 5 Hz).

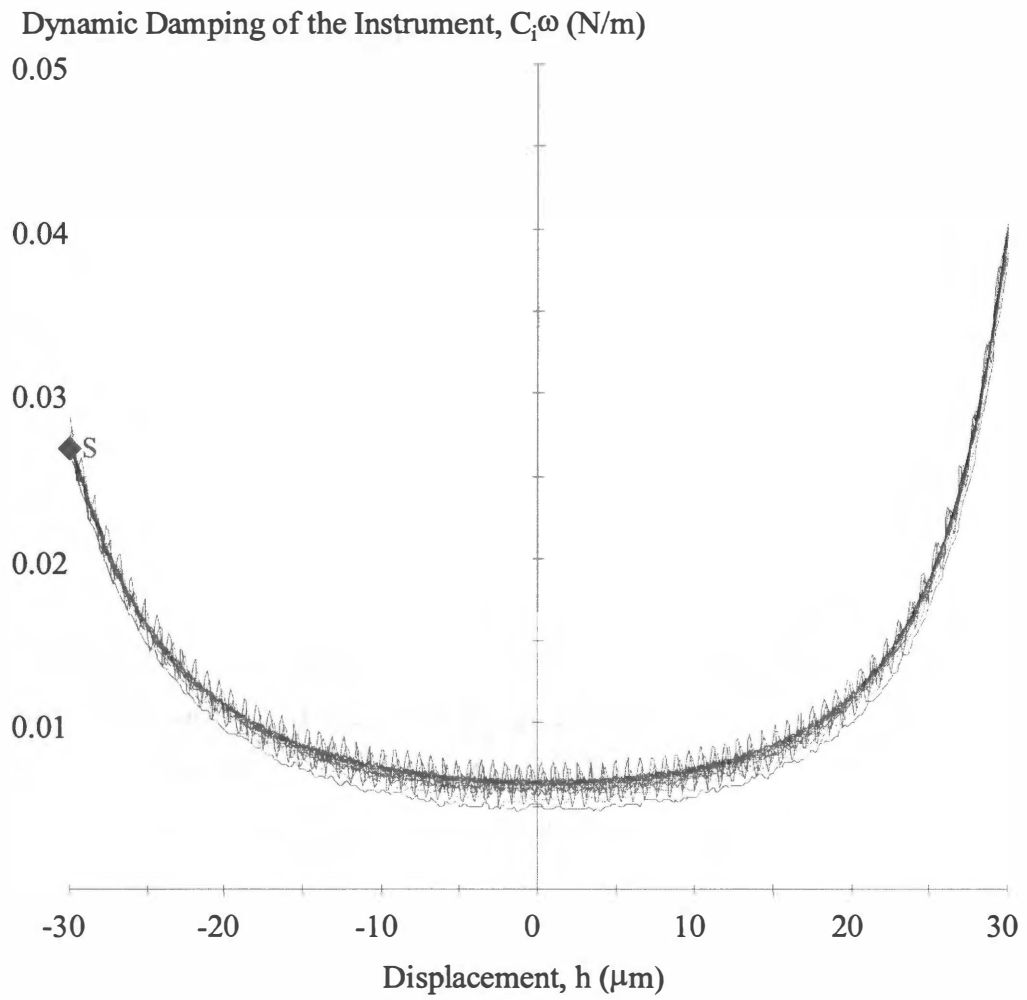


Figure 29. Dynamic damping of the instrument versus displacement of the indenter at various frequencies (from 30 to 200 Hz every 5 Hz).

$$A(h_c) = 24.5h_c^2 \quad (47)$$

Thus, the contact stiffness and damping defined by equations (39) and (40) increase linearly as a function of the contact depth, as shown in Figure 30. Consequently, the Berkovich indenter is very sensitive to contact detection and allows for very small contacts.

For the flat punch indenter, the area of contact should be constant and defined as:

$$A = \pi \left(\frac{D}{2} \right)^2 \quad (48)$$

where D is the diameter of the flat punch. Thus, the contact stiffness and damping should also be constant and independent of the depth of penetration. Figure 31 shows that after a certain load, these quantities are indeed constant. The small range of displacement over which the contact stiffness and damping rise to the contact value is explained by a slight misalignment of the tip and the surface, as well as surface morphology.

A major drawback in using the Berkovich indenter is that the contact area changes when the load on the indenter is held constant due to viscous deformation of the material. Because the flat punch does not suffer from this problem, it can be used to provide frequency sweeps at constant contact area.

4.2.2 BERKOVICH

A special experimental method was written to characterize the viscoelastic

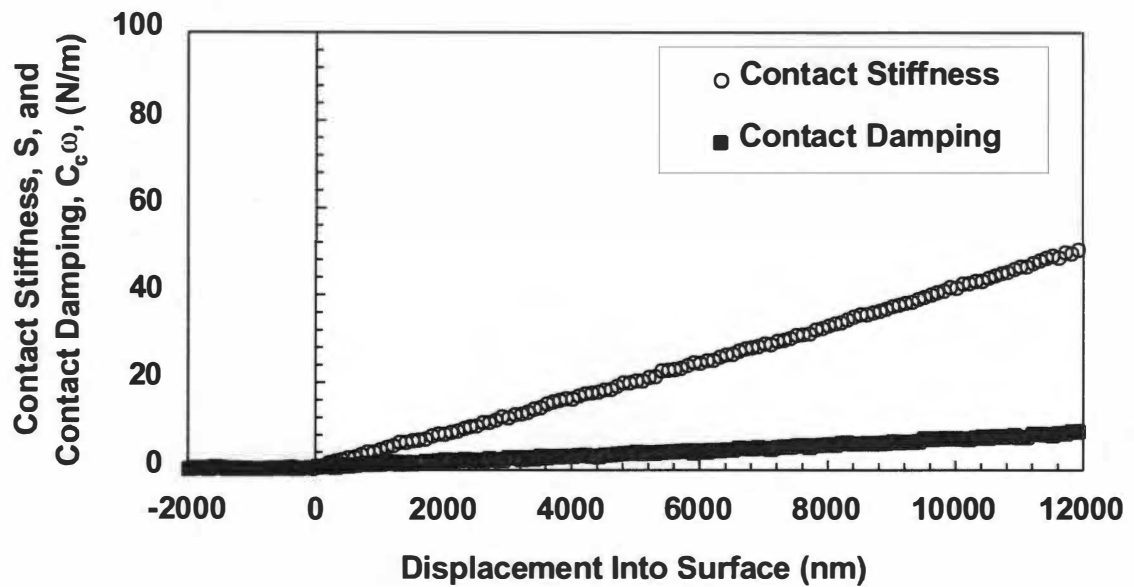


Figure 30. A plot of contact stiffness and contact damping versus penetration for polydimethylsiloxane using a Berkovich indenter.

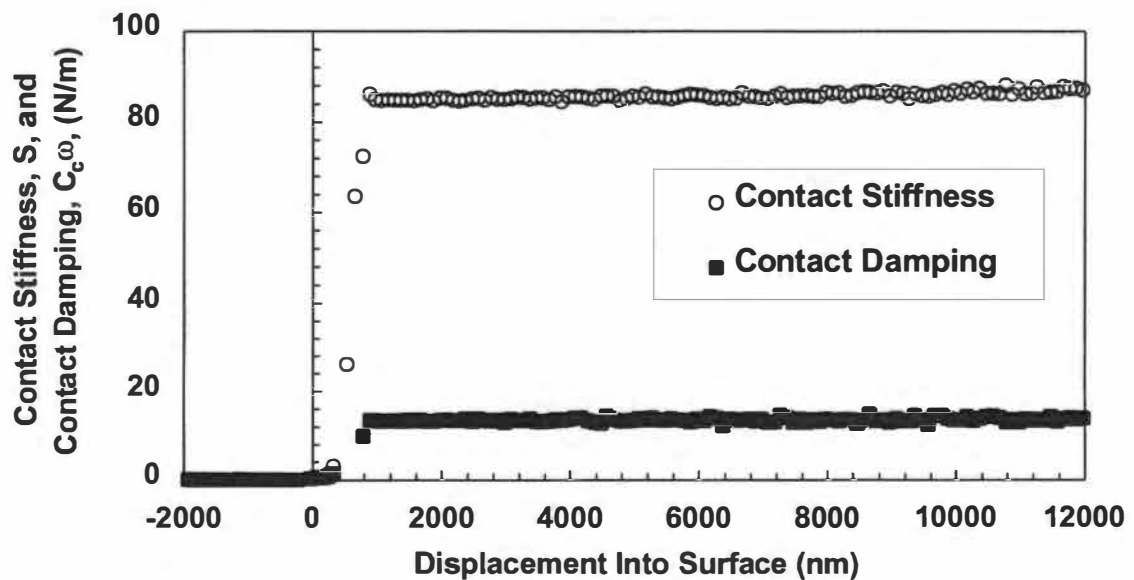


Figure 31. A plot of contact stiffness and contact damping versus penetration for polydimethylsiloxane using a flat punch indenter.

properties of soft materials using the Berkovich indenter. The method allows users to measure the storage and loss modulus and the loss tangent of soft polymer materials at specific frequencies.

The indentation measurements were conducted at a constant loading rate $(\dot{P}/P)$ [6, 14] of 0.05 s^{-1} . Ten indentations were made at each frequency and on each material. The data from all ten indentations were then discretized into finite displacement windows and averaged to obtain a mean and standard deviation for all indentations. As a result, these measurements gave the viscoelastic properties as a function of the penetration depth. Such results were determined for each frequency.

Description of the experimental method for a Berkovich indenter

To perform a test, the required inputs are:

- ✓ Delta X and Y for finding surface: distance from the test location where the surface find is performed.
- ✓ Surface approach distance: distance from the surface where the approach starts.
- ✓ Surface approach sensitivity: sensitivity of the contact stiffness for the surface detection.
- ✓ Surface approach velocity: velocity of the indenter during the approach to the surface.
- ✓ Surface approach to store: distance of the approach kept at the end of the test.
- ✓ Depth limit: depth at which the loading stops.
- ✓ Strain rate: define the load rate applied on the indenter during the loading process. It is increased such that the load rate is proportional to the load:

$$\frac{\dot{P}}{P} = c. \text{ The parameter } c \text{ sets the strain rate during the test.}$$

- ✓ Sample frequency: frequency used for the test.
- ✓ Test location: location where the test is performed.

Table Motion

The sample moves to the test location plus the delta X and Y for finding surface.

Surface Finding Procedure

The DCM head moves down while the indenter displacement signal reads at 7 μm . The head stops when the displacement reaches 6 μm , showing that the indenter has touched the surface. The indenter is brought up to -20 μm . The sample moves half the way to the test location. The indenter approaches the surface at a fast velocity to estimate the height of the surface. When the indenter touches the surface, it is raised to the surface approach distance.

Approach

Slowly, at the surface approach velocity, the indenter searches for contact with the sample surface. Contact is detected when the contact stiffness reaches a value defined by the surface approach sensitivity.

Loading

At contact, the load applied on the indenter is increased such that $\dot{P}/P$ stays constant. This loading segment ends when the penetration reaches the depth limit, or the load exceeds 10 mN (the hardware load limit).

Unloading

The load is held constant at its maximum value for 10 seconds, and then is decreased linearly at a rate calculated from the loading rate at the end of the loading. When unloading is complete, the head is brought to its top position.

4.2.3 FLAT PUNCH

A separate experimental method was written to characterize the viscoelastic properties of soft materials using the flat punch indenter. The method allows users to measure the storage and loss modulus and the loss tangent of soft polymer materials at various frequencies during a single indentation test. These properties are calculated from the equations (12) and (13) using the known area of contact, A , for the flat punch:

$$A = \pi \frac{D^2}{4} \quad (49)$$

where D is the diameter of the flat punch. The storage modulus, E' , and the loss modulus, E'' , are then calculated with

$$E' = \frac{S}{D} \quad (50)$$

and

$$E'' = \frac{C_c \omega}{D} \quad (51)$$

where S is the contact stiffness, C_c is the contact damping, and ω is the angular frequency. The loss tangent is still defined by equation (14).

Ten indentations were made on each material. The indenter was driven in and held at a constant depth of 5 μm . Dynamic properties were then measured while the frequency was swept from 4 to 256 Hz. The data from the ten

indentations were discretized into finite frequency windows and averaged to obtain a mean and standard deviation for all the indentations. As a result, the measurements gave the viscoelastic properties as a function of the frequency.

Description of the experimental method for a flat punch indenter

To perform a test, the required inputs are:

- ✓ Delta X and Y for finding surface: distance from the test location where the surface find is performed.
- ✓ Surface approach sensitivity: sensitivity of the contact stiffness for the surface detection.
- ✓ Surface approach velocity: velocity of the indenter during the approach to the surface.
- ✓ Depth limit: depth at which the loading stops.
- ✓ Frequency step coefficient: step used between each frequency. The new frequency is the previous frequency multiplied by the step.
- ✓ Starting frequency: first frequency tested.
- ✓ Ending frequency: last frequency tested.
- ✓ Test location: location where the test is performed.

Table Motion

The sample moves to the test location plus the delta X and Y for finding surface.

Surface Finding Procedure

The DCM head moves down while the indenter displacement signal reads at 7 μm . The head stops when the displacement reaches 6 μm , showing that the indenter has touched the surface. The indenter is brought up to -20 μm . The sample moves to the test location.

Approach

The indenter approaches the surface at the surface approach velocity (fast). Contact is detected when the contact stiffness reaches a value defined by the surface approach sensitivity.

Loading

At contact, the indenter continues to be driven into the material at the same velocity until the depth limit is reached, or the load exceeds 10 mN (the hardware load limit).

Measurement

While the penetration depth is held constant, the frequency is set and the phase calibration is set as a function of this frequency. Then the storage and loss modulus, and loss tangent, are recorded for a few seconds. The frequency is incremented by a multiple of the previous frequency by the frequency step. This is continued as long as the frequency is lower than the final frequency.

Unloading

The load is held constant at its maximum value for 10 seconds, and then is decreased linearly at the same velocity as the approach. When unloading is complete, the head is brought to its top position.

4.3 DMA TESTS

The DMA tests were performed using a DMTA VTM at room temperature (24°C). Two different deformation modes were used for the tests: compression and tension. Polyurethane (PU) and polydimethylsiloxane (PDMS) samples were tested at various frequencies.

To begin a test, it was first necessary to determine the value of the static force necessary for the test. This was accomplished by measuring the storage modulus as a function of the static force, for a constant dynamic strain and

frequency. The value of the static force was taken at the level of the plateau (see section 5.3). It was also necessary to determine the value of the dynamic strain needed to stay in the linear viscoelasticity region. This was accomplished by measuring the storage modulus as a function of the dynamic strain for the static force value found previously and at constant frequency. Then this test was repeated at the lowest and highest frequencies needed to verify the dynamic strain over the entire frequency range. Finally, the storage and loss moduli and the loss tangent were measured as a function of the frequency for the appropriate values of the static force and the dynamic strain.

The first DMA tests on both materials revealed that for some deformation modes and/or sample geometries, the DMA results were very different from the indentation results. To understand this behavior, DMA experiments were conducted with several different specimen configurations (single layer and several layers of material) and deformation modes (tension and compression). An analysis of the results revealed that DMA measurements are very sensitive to the sample geometry and to the deformation mode (see Chapter 5).

Different specimen configurations were chosen for each deformation mode. For the tests on the polyurethane, the configurations are presented in Figure 32. Two compression tests (one layer and two layers of PU), a tension test, and a compression test using the tension fixture were all used. For polydimethylsiloxane, the configurations are presented in Figure 33. They consisted of two compression tests (one layer and three layers of PDMS), a tension test, and a compression test using the tension fixture. All dimensions for the samples will be presented in Chapter 5 (Tables 1 and 2).

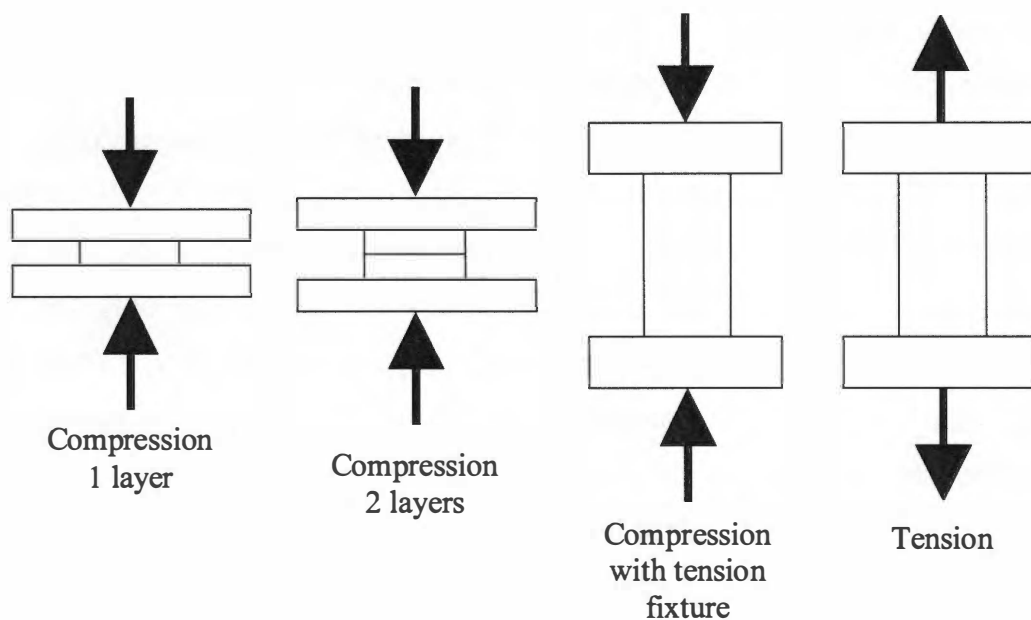


Figure 32. A schematic of the different specimen configurations for DMA tests on the polyurethane.

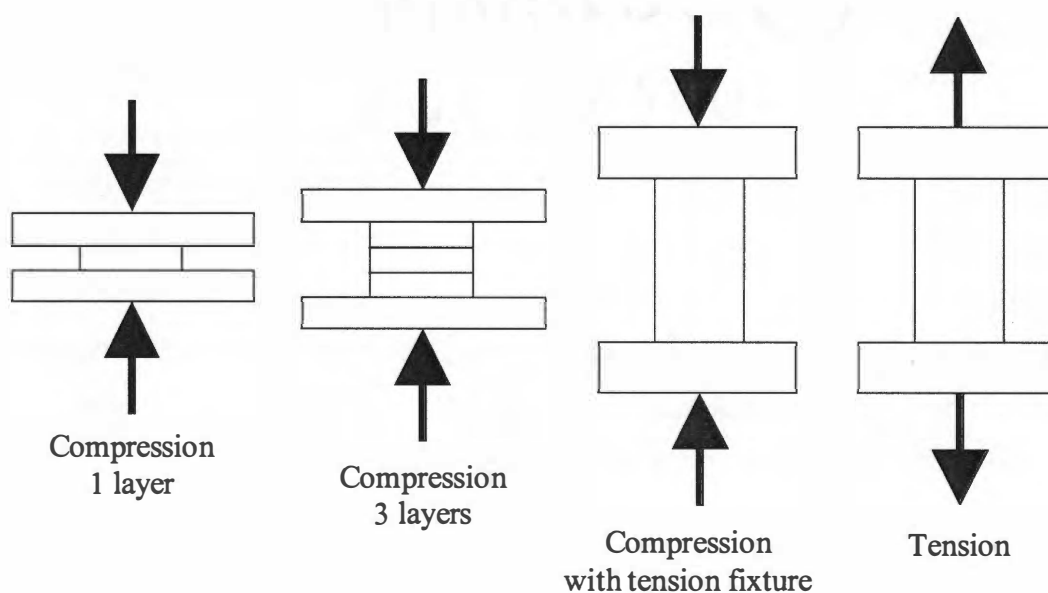


Figure 33. A schematic of the different specimen configurations for DMA tests on the polydimethylsiloxane.

4.4 PREPARATION OF THE SAMPLES

The two materials tested in the study were a polyurethane and a polydimethylsiloxane. Both materials are completely amorphous and rubbery at room temperature, and therefore isotropic. Polyurethane elastomers are characterized in the literature by a tensile modulus range from 1400 psi to 3200 psi [18].

The polyurethane and polydimethylsiloxane were obtained in sheet form; the thickness for the polyurethane was 2.06 mm and for the polydimethylsiloxane, 0.89 mm. The roughness of the sample surfaces was not measured, but was not expected to affect the results due to the large depths of indentation used for the study.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 PRECISION AND ACCURACY OF INDENTATION MEASUREMENTS

In order to test very soft materials with the Nano Indenter[®] DCM, several experimental issues were addressed: phase angle measurement, determination of the dynamic stiffness and damping of the instrument, and the procedure for detection of first contact between the indenter and the material surface.

The correction procedure for the phase angle was described in section 4.1.1. This correction defined the correct phase angle as that calculated from the dynamic compliance measurements. The error in phase angle versus frequency, presented in Figure 34, shows the results of this correction. The phase angle correction allows it to be measured at any frequency from 1 Hz to 250 Hz within 0.4 degrees.

Using the phase angle correction, improvements in the determination of the dynamic stiffness and damping of the instrument were made as described in section 4.1.2. This leads to improvements in the accuracy and precision of the dynamic behavior of the instrument over the frequency and displacement range. The frequency range for accurate calibrations was extended from 4 to 256 Hz.

Furthermore, a precise detection of the first contact between the indenter and the material surface, crucial for Berkovich indentation on very soft materials, was made possible with the new dynamic calibration of the instrument and the phase angle correction. Figures 35 and 36 show the noise in the contact stiffness and damping before and after contact for five different tests at 32 Hz. The improvements reduced the noise level from ± 10 N/m to the order of ± 1 N/m, thereby facilitating more precise determination of initial surface contact.

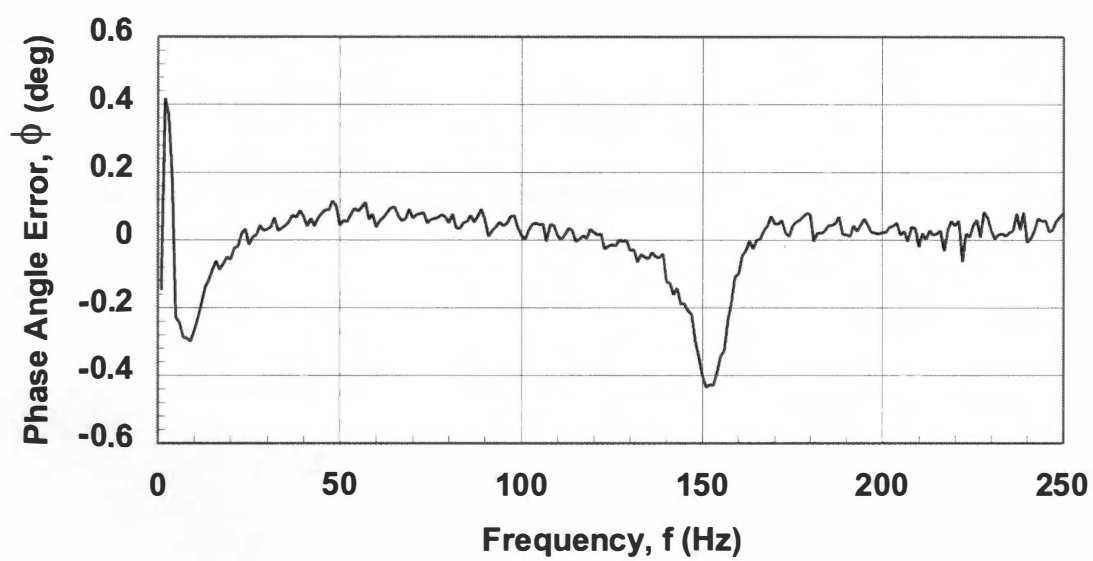


Figure 34. Phase angle error versus frequency after phase angle correction.

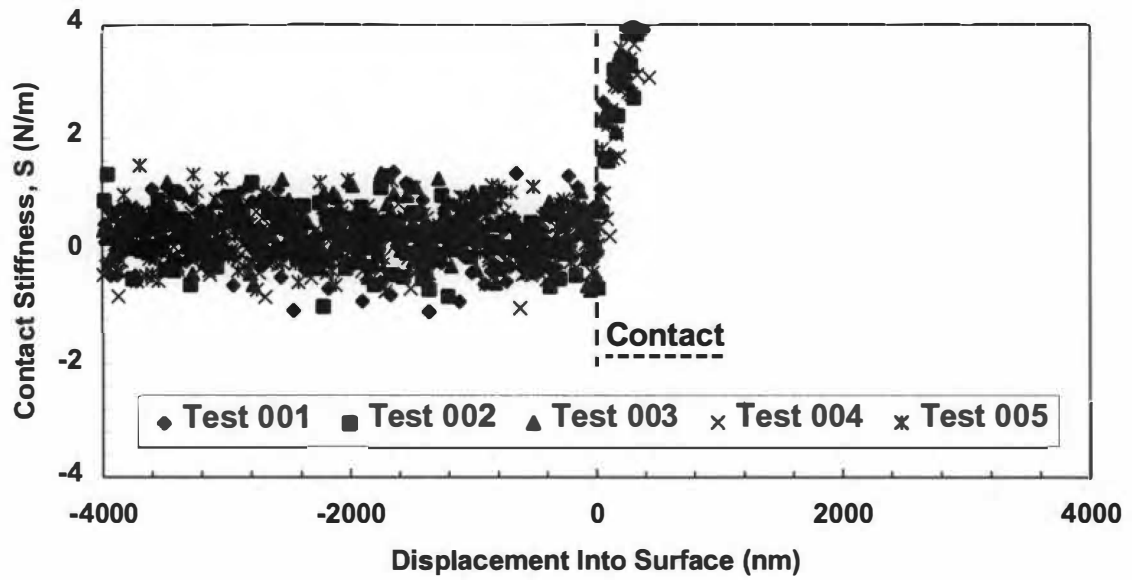


Figure 35. A plot of the contact stiffness versus penetration for five tests on polydimethylsiloxane.

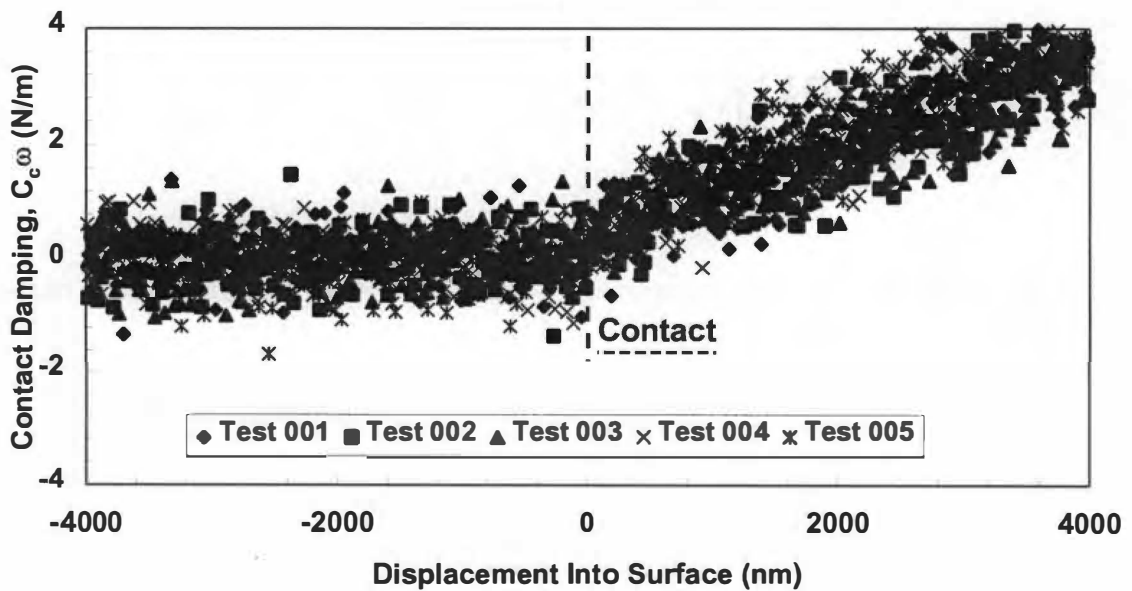


Figure 36. A plot of the contact damping versus penetration for five tests on polydimethylsiloxane.

5.2 INDENTATION RESULTS USING BERKOVICH AND FLAT PUNCH INDENTER

Viscoelastic properties for polyurethane and polydimethylsiloxane were measured by indentation testing at frequencies from 4 Hz to 256 Hz. The tests using the Berkovich indenter gave viscoelastic measurements as a function of the penetration depth and frequency, while tests using the flat punch indenter gave more complete viscoelastic measurements as a function of frequency. In order to compare the Berkovich and flat punch results, the viscoelastic properties for the Berkovich indentations were measured at the same area of contact as the flat punch indentations, i.e., $6221 \mu\text{m}^2$. This area of contact corresponds to a depth of about $19 \mu\text{m}$ for the Berkovich indentations.

5.2.1 INDENTATION OF POLYURETHANE

The frequency dependences of the viscoelastic properties of polyurethane are presented in Figures 37 - 39. Each plot includes results using both the Berkovich and the flat punch indenters.

Figure 37 shows that the storage modulus increases significantly over the range of frequency investigated. The results for the two different indenter tips are similar.

Figure 38 shows the frequency dependence of the loss modulus. As for the storage modulus, the loss modulus increases as a function of frequency and shows a large change over the range of frequency investigated. Again, the results given by the two different indenter tips are similar.

Figure 39 shows the frequency dependence of the loss tangent of the polyurethane. The loss tangent increases as a function of frequency, reaching a

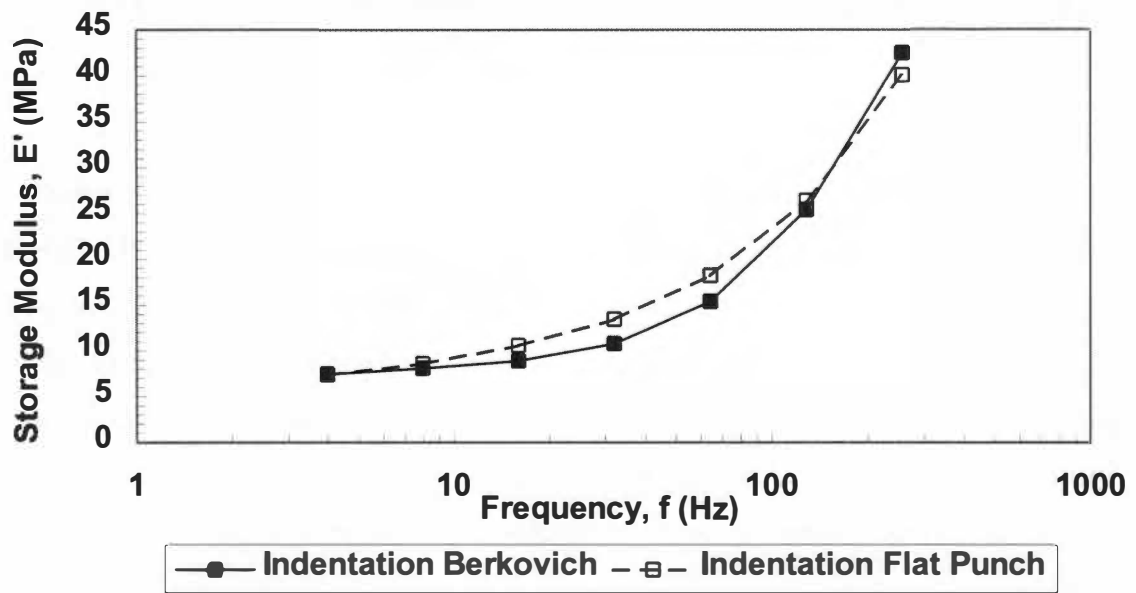


Figure 37. A plot of storage modulus versus frequency for polyurethane using both Berkovich and flat punch indenters.

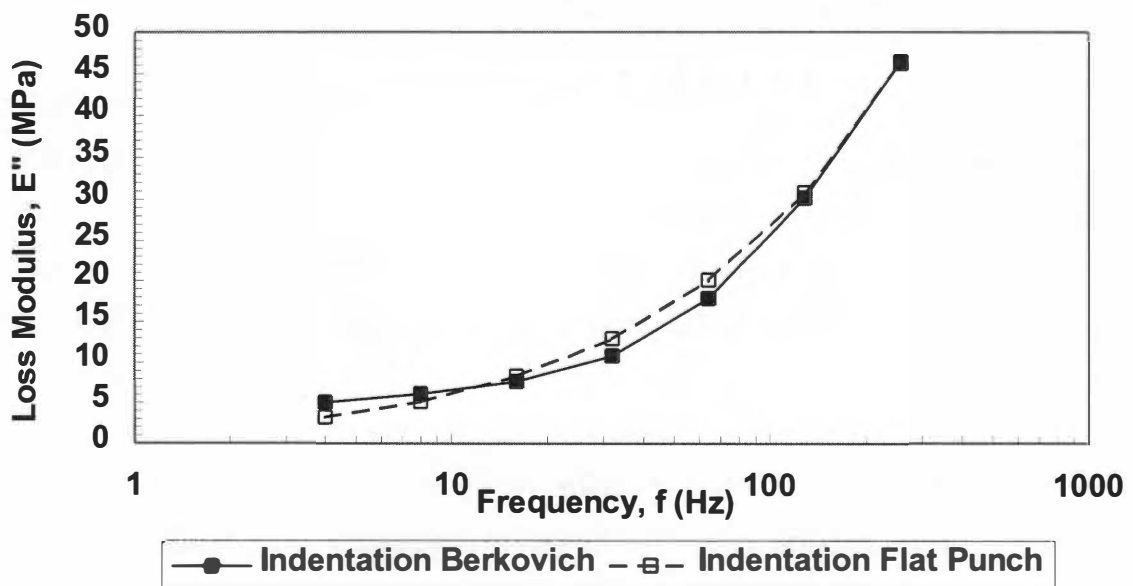


Figure 38. A plot of loss modulus versus frequency for polyurethane using both Berkovich and flat punch indenters.

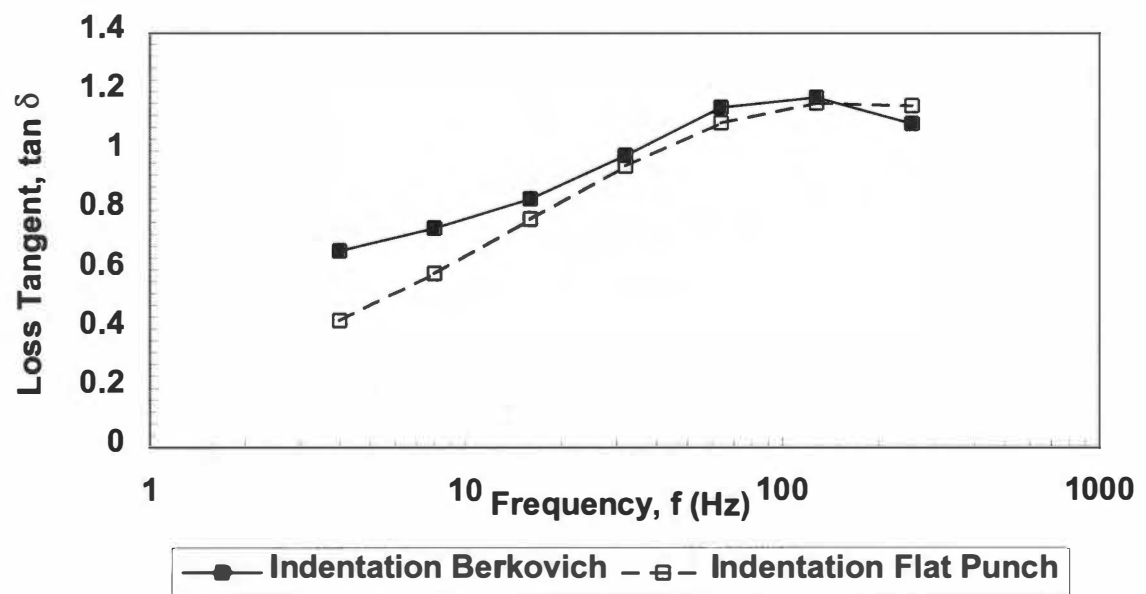


Figure 39. A plot of loss tangent versus frequency for polyurethane using both Berkovich and flat punch indenters.

maximum at about 100 Hz, and then starts to decrease. Although the loss tangent shows slight differences from one tip to the other at low frequencies, the trends are similar, and the values are nearly the same, especially at frequencies near the maximum.

5.2.2 INDENTATION OF POLYDIMETHYLSILOXANE

Indentation measurement results for polydimethylsiloxane are presented in Figures 40 - 42. Figure 40 shows the frequency dependence of the storage modulus. The storage modulus increases slightly as a function of frequency, but generally remains fairly constant over the range of frequency investigated. The results given by the two different indenter tips are essentially the same. It is notable that a storage modulus of less than 2 MPa can be measured by this technique with both the Berkovich and flat punch indenters.

Figure 41 shows the frequency dependence of the loss modulus for polydimethylsiloxane. Like the storage modulus, the loss modulus increases as a function of frequency. Even though the results given by the two different tips show slight differences, the trends are consistent.

Finally, Figure 42 shows the frequency dependence of the loss tangent for polydimethylsiloxane. The loss tangent increases as a function of frequency. As for the loss modulus, the loss tangent shows slight differences from one tip to the other all over the range of frequency investigated. However, the trends exhibited by the two tips are the same.

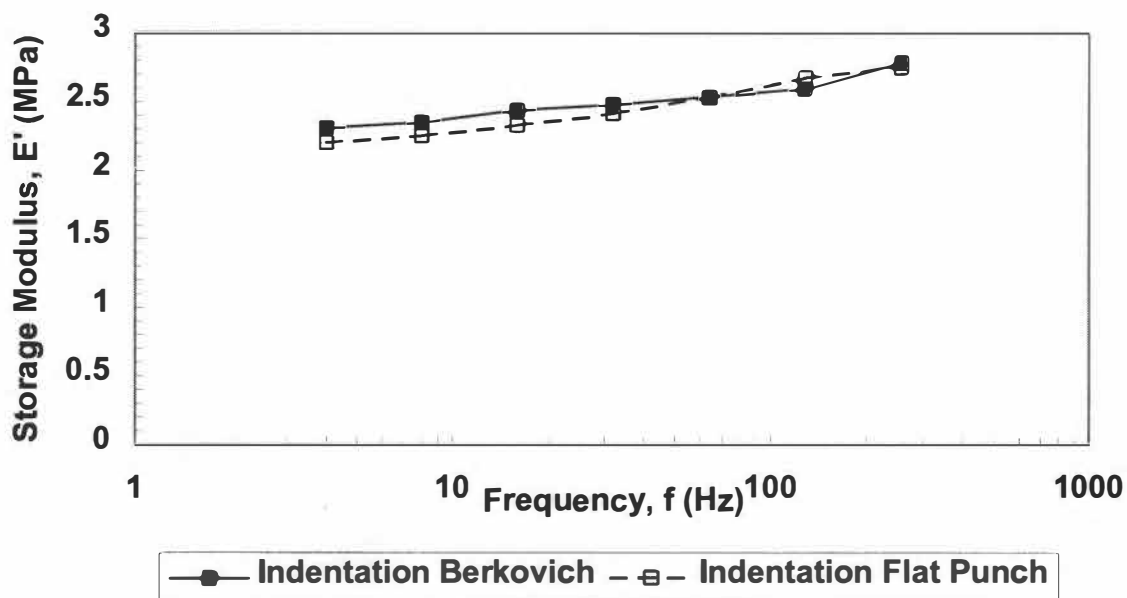


Figure 40. A plot of storage modulus versus frequency for polydimethylsiloxane using both Berkovich and flat punch indenters.

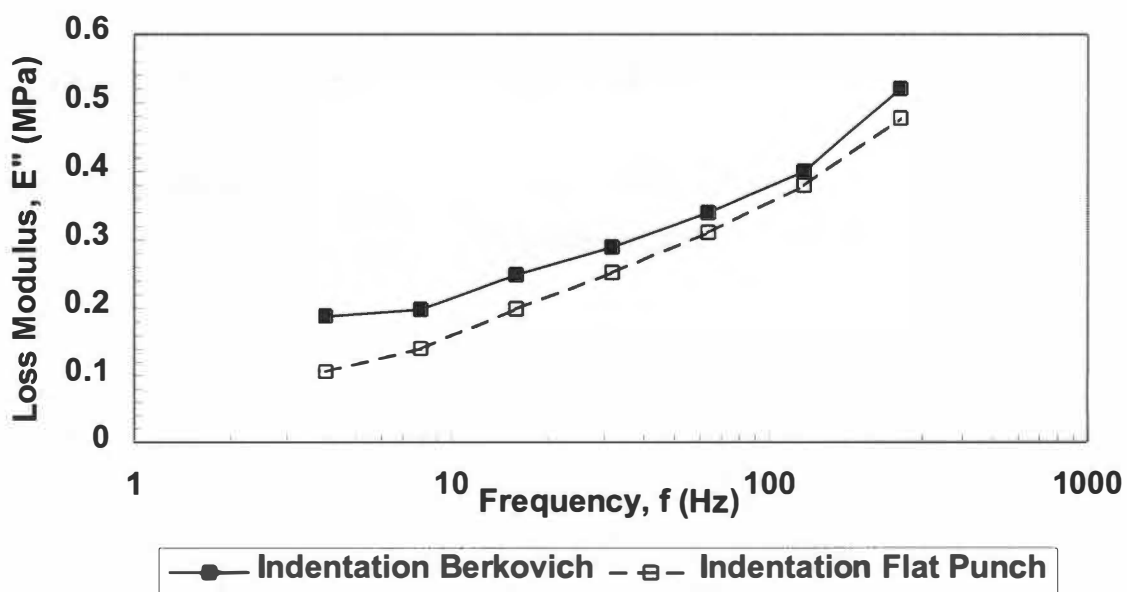


Figure 41. A plot of loss modulus versus frequency for polydimethylsiloxane using both Berkovich and flat punch indenters.

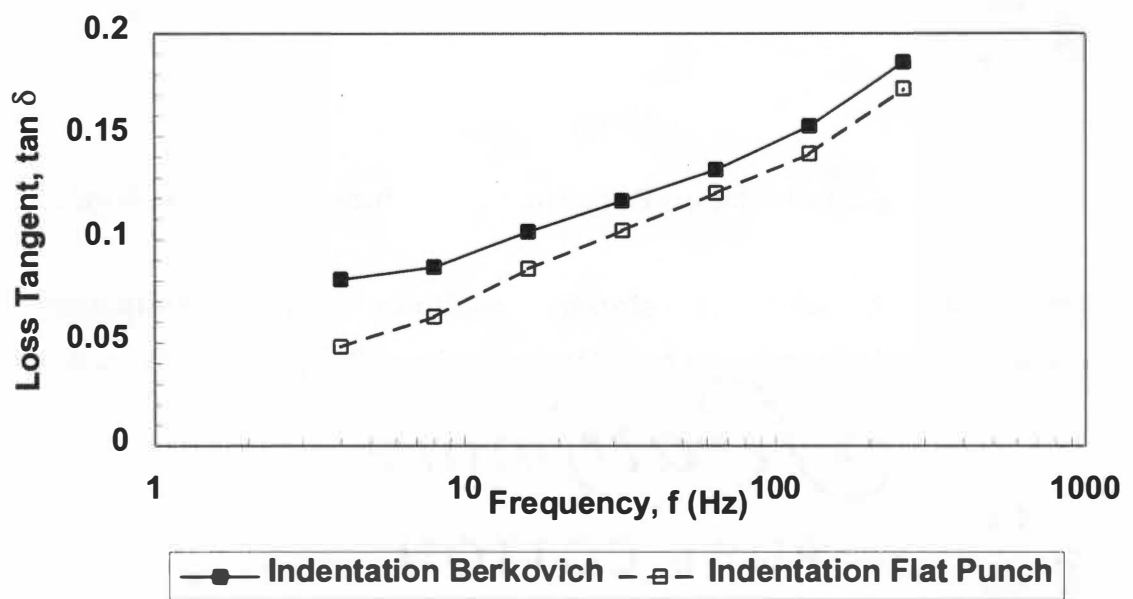


Figure 42. A plot of loss tangent versus frequency for polydimethylsiloxane using both Berkovich and flat punch indenters.

5.3 DMA RESULTS IN COMPRESSION AND TENSION

Dynamic mechanical analysis was used to measure the viscoelastic properties for polyurethane and polydimethylsiloxane for frequencies from 1 Hz to 200 Hz. Two different deformation modes were used for the tests: compression and tension. The test procedures were described in section 4.3.

An analysis of the machine response without a sample (free-hanging instrument) led to the conclusion that DMA measurements over 40 Hz may not be accurate for the two very soft polymeric materials tested. Indeed, an apparent decrease of the viscoelastic properties at frequencies greater than 40 Hz is due to the passage of a resonance in the testing apparatus.

5.3.1 DMA RESULTS FOR POLYURETHANE

Four different DMA tests were performed on polyurethane, as shown on Figure 32. They included:

- Tension fixture
 - Tension mode
 - Compression mode
- Compression fixture
 - Compression mode with one layer of PU
 - Compression mode with two layers of PU

Figure 43 shows two plots of the storage modulus versus the static force (linear and logarithmic scales) for polyurethane, with a constant dynamic strain of 0.05% and a constant frequency of 1Hz. Other results are presented in Figures 44 - 46. For the tension mode and compression mode using the tension fixture, the storage modulus shown in the logarithmic plot in Figure 43 stays relatively

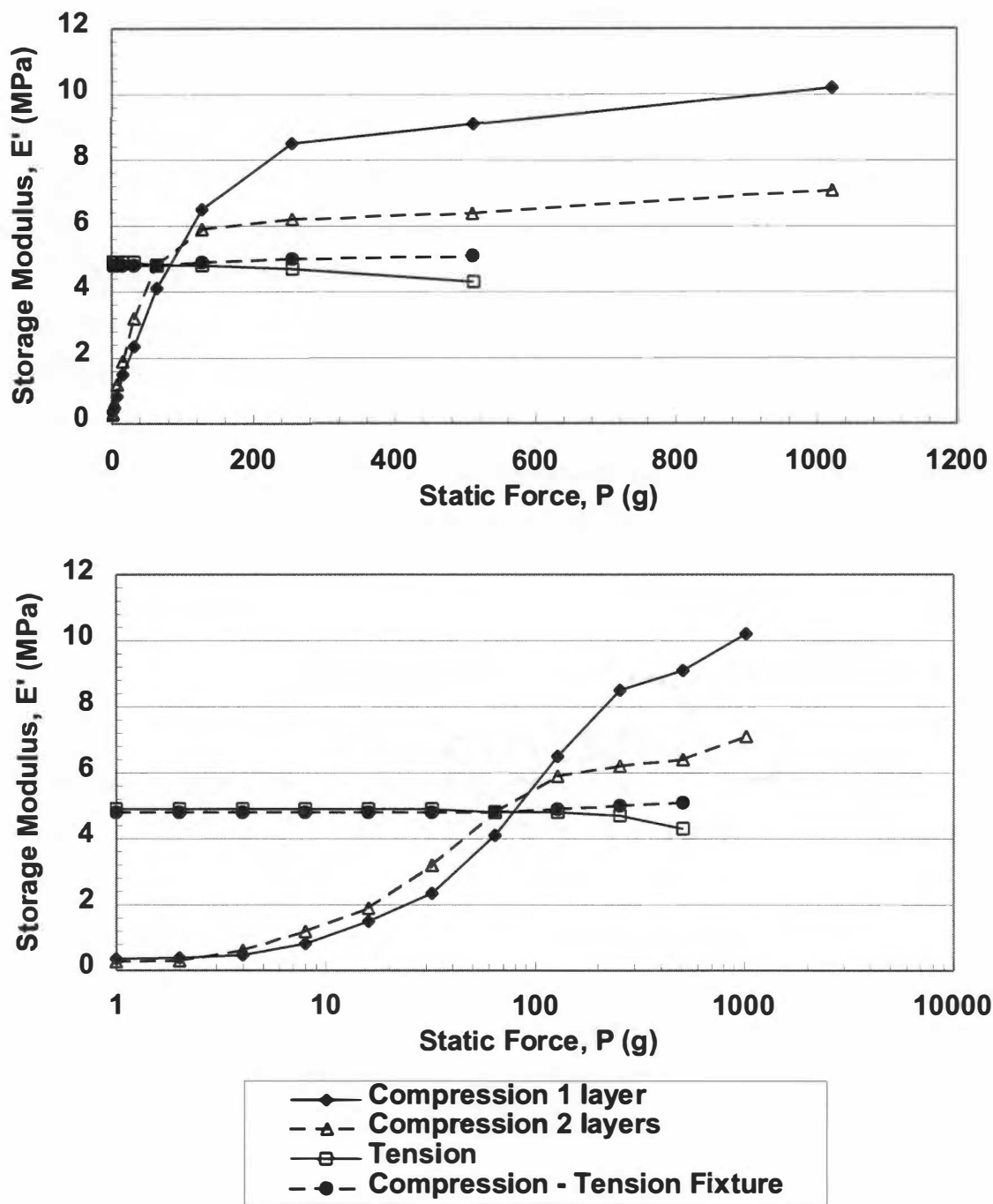


Figure 43. Two plots of storage modulus versus static force (linear and logarithmic scales) for polyurethane using the DMA technique, with a constant dynamic strain of 0.05% and a constant frequency of 1 Hz.

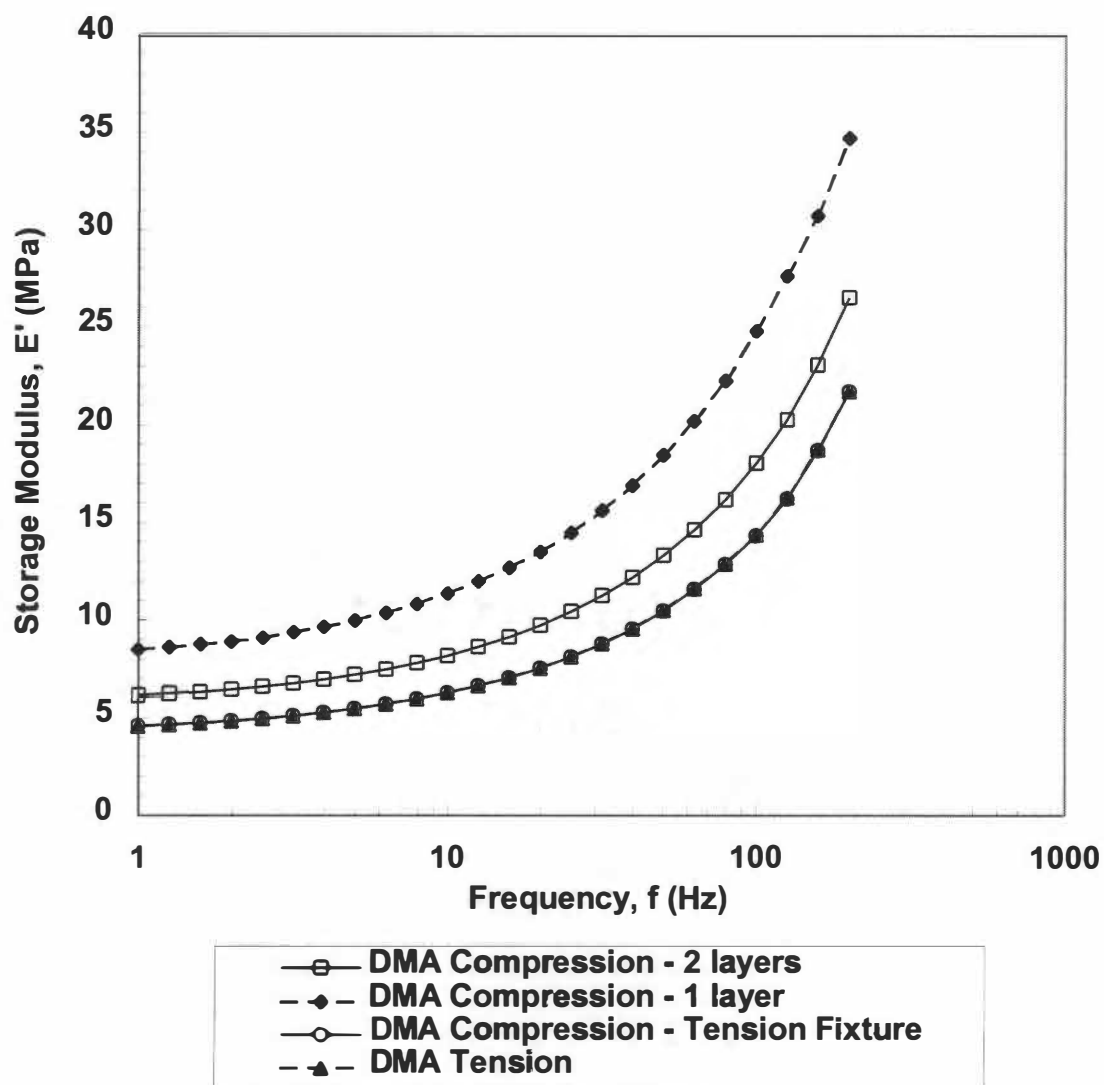


Figure 44. A plot of storage modulus versus frequency for polyurethane using the DMA technique with a constant dynamic strain of 0.05%.

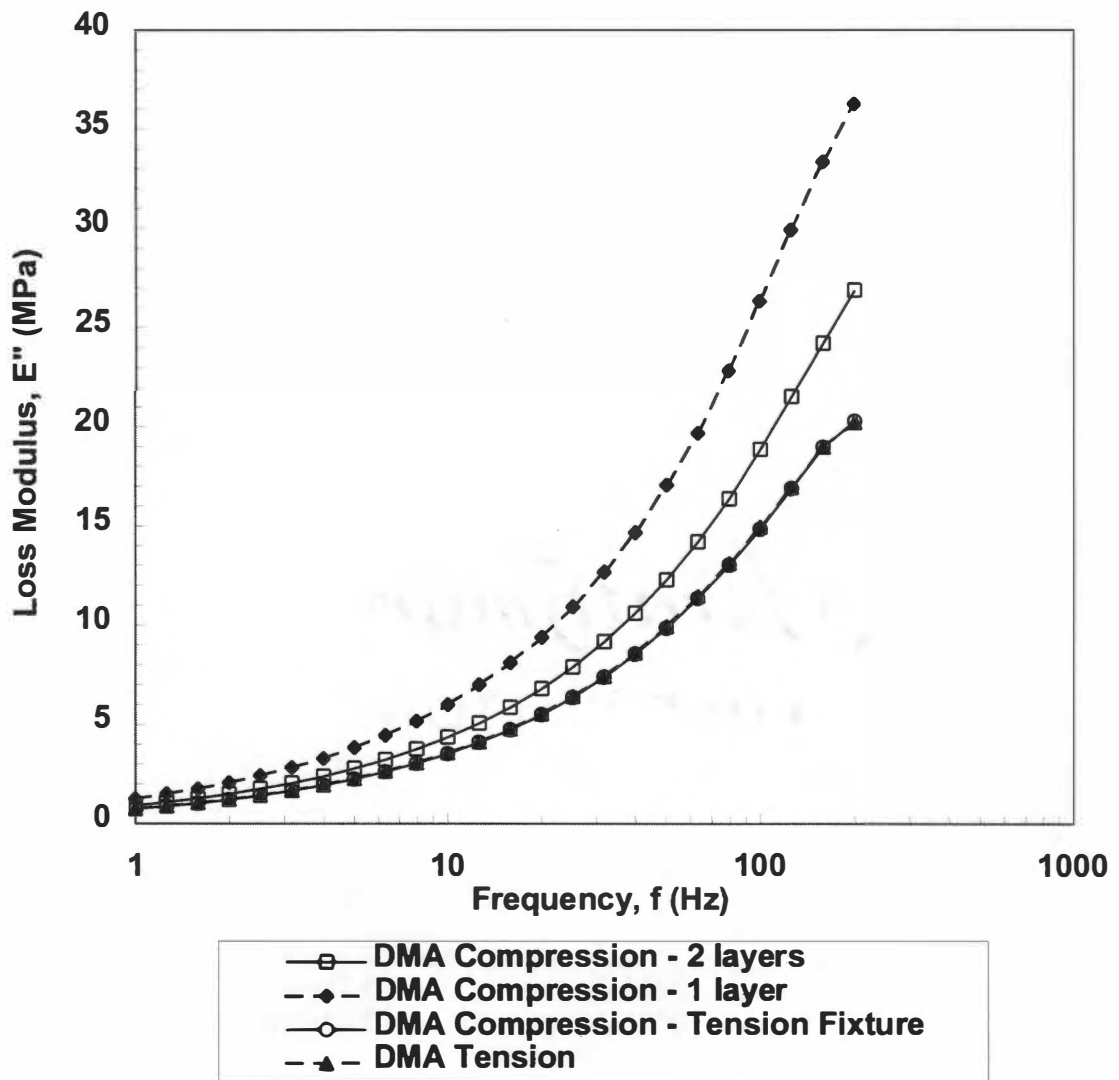


Figure 45. A plot of loss modulus versus frequency for polyurethane using the DMA technique with a constant dynamic strain of 0.05%.

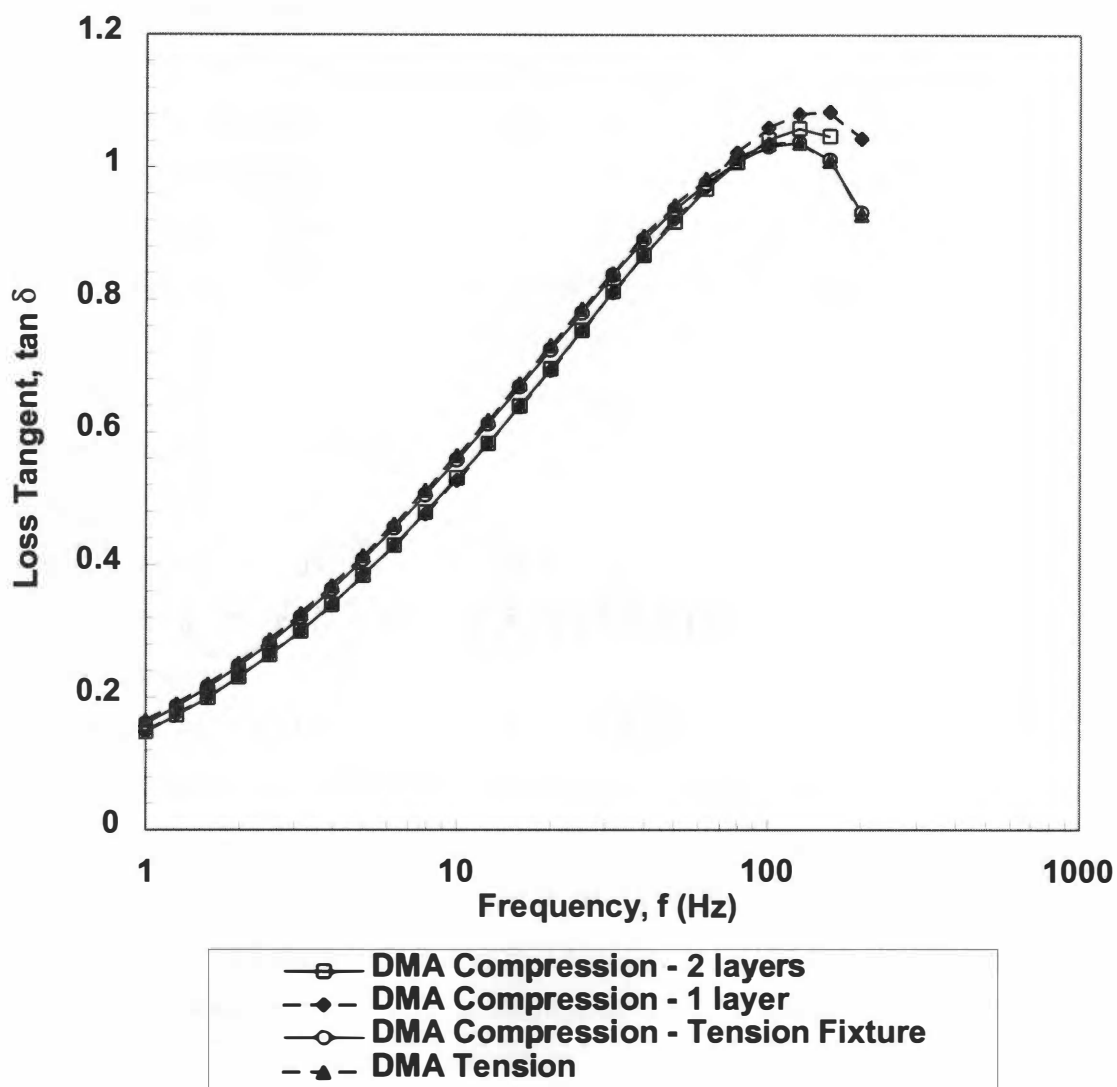


Figure 46. A plot of loss tangent versus frequency for polyurethane using the DMA technique with a constant dynamic strain of 0.05%.

constant whatever the static force value. The value of the static force used for the tests using the tension fixture shown in Figures 44 – 46 was then taken at 10 g (0.1 N). For the compression fixture with one and two layers, the storage modulus shown in the linear plot in Figure 43 increases with the static force and seems to reach a plateau around 300 g (3 N). This rise in modulus at shallow depths is due to misalignment between the specimen and the compression platters as will be discussed in section 5.4.1. The value of the static force used for the test using the compression fixture shown in Figures 44 – 46 was then taken at 400 g (4 N). In order to maintain the dynamic strain in the linear viscoelasticity region, a dynamic strain of 0.05% was used in all tests.

Figures 44 and 45 show plots of storage and loss moduli versus frequency for polyurethane using the DMA technique. As a general observation, the storage and loss moduli show the same trends for all the modes and fixtures used in the test; the storage and loss moduli increase as a function of the frequency and show a large change over the range of frequency used. Results for storage and loss moduli obtained using the tension fixture, i.e., in tension and compression mode, are essentially the same. However, the storage and loss moduli measured using the compression fixture with one and two layers of material are higher than the results with the tension fixture. Furthermore, the compression results with one layer of material are higher than those with two layers of material. An explanation of this effect will be given in sections 5.4.1 and 5.4.2.

Figure 46 shows a plot of loss tangent versus frequency for polyurethane using the DMA technique. The distinct differences in the storage and loss moduli observed for each of the different deformation modes do not appear in the loss tangent. This is due to the fact that the loss tangent measurement is independent of the fixture mode and the geometry of the sample. The loss tangent increases as a function of frequency, reaches a maximum, and then starts to decrease. Moreover, it shows also a very large change over the range of frequency used.

5.3.2 DMA RESULTS FOR POLYDIMETHYLSILOXANE

Four different DMA tests were performed on polydimethylsiloxane, as shown in Figure 33. They included:

- Tension fixture
 - Tension mode
 - Compression mode
- Compression fixture
 - Compression mode with three layers of PDMS with $P=1\text{g}$ (0.01 N)
 - Compression mode with three layers of PDMS with $P=200\text{g}$ (2 N)

Figure 47 shows a plot of the storage modulus versus the static force (linear and logarithmic scales) for polydimethylsiloxane, with a constant dynamic strain of 0.05% and a constant frequency of 1Hz. The viscoelastic properties for polydimethylsiloxane as a function of the frequency are presented in Figures 48 - 50. For the tension mode and compression mode using the tension fixture, the storage modulus shown in the logarithmic plot in Figure 47 stays relatively constant whatever the static force. Thus, the static force, used for tests using the tension fixture in Figures 48 – 50, was taken as 10 g (0.1 N). As it was for the polyurethane, for the compression fixture with three layers of polydimethylsiloxane, the storage modulus shown in the linear plot in Figure 47 increases with the static force and seems to reach a plateau around 100 g (1 N). However, the results for only one layer of material do not reach a plateau; these results will be discussed in detail in sections 5.4.1 and 5.4.2. Again, the rise in modulus at shallow depths is due to misalignment between the specimen and the compression disks, and so there is an increase of the contact area. Therefore, for

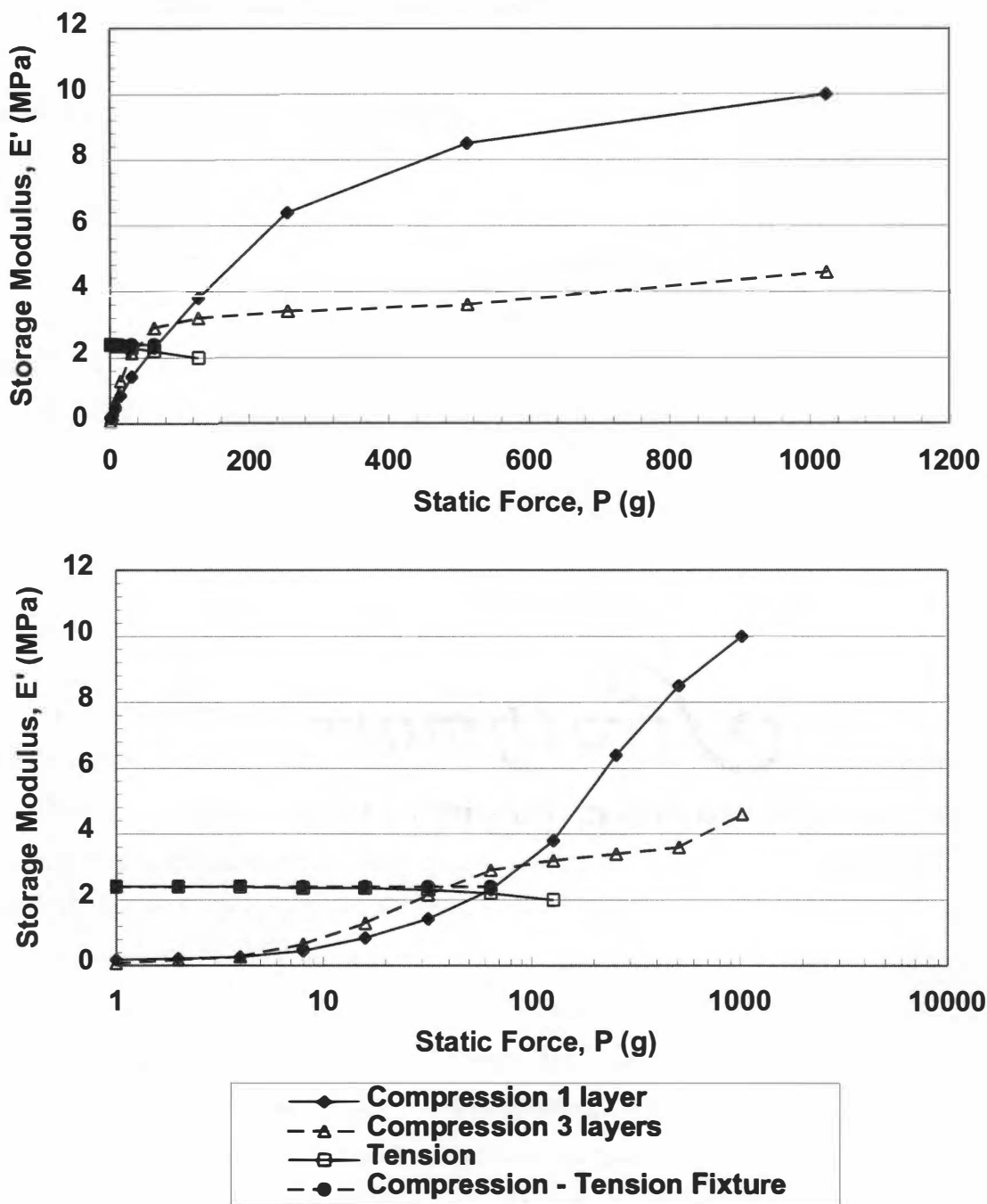


Figure 47. Two plots of storage modulus versus frequency (linear and logarithmic scales) for polydimethylsiloxane using the DMA technique, with a constant dynamic strain of 0.05% and a constant frequency of 1Hz.

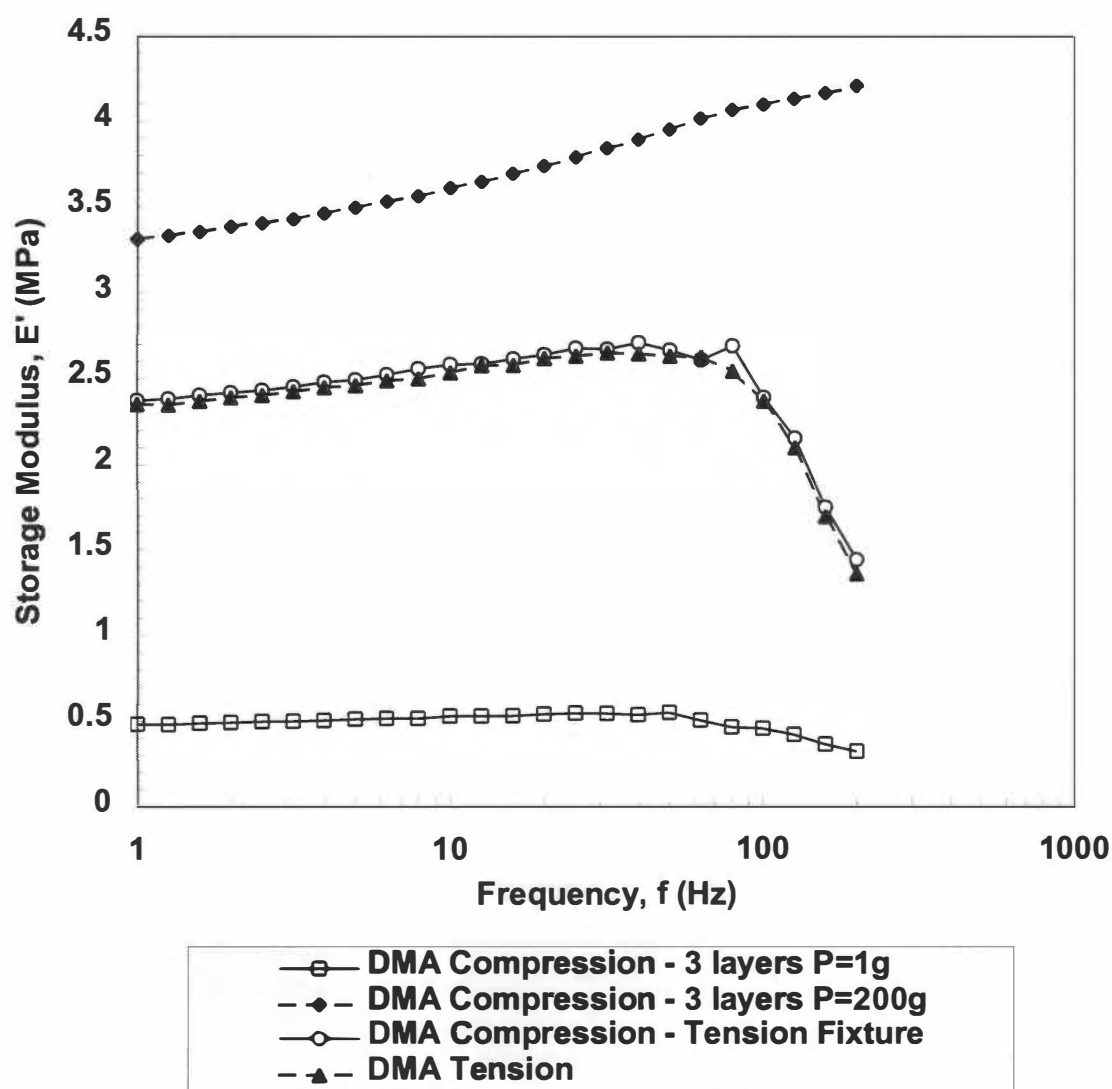


Figure 48. A plot of storage modulus versus frequency for polydimethylsiloxane using the DMA technique with a constant dynamic strain of 0.05%.

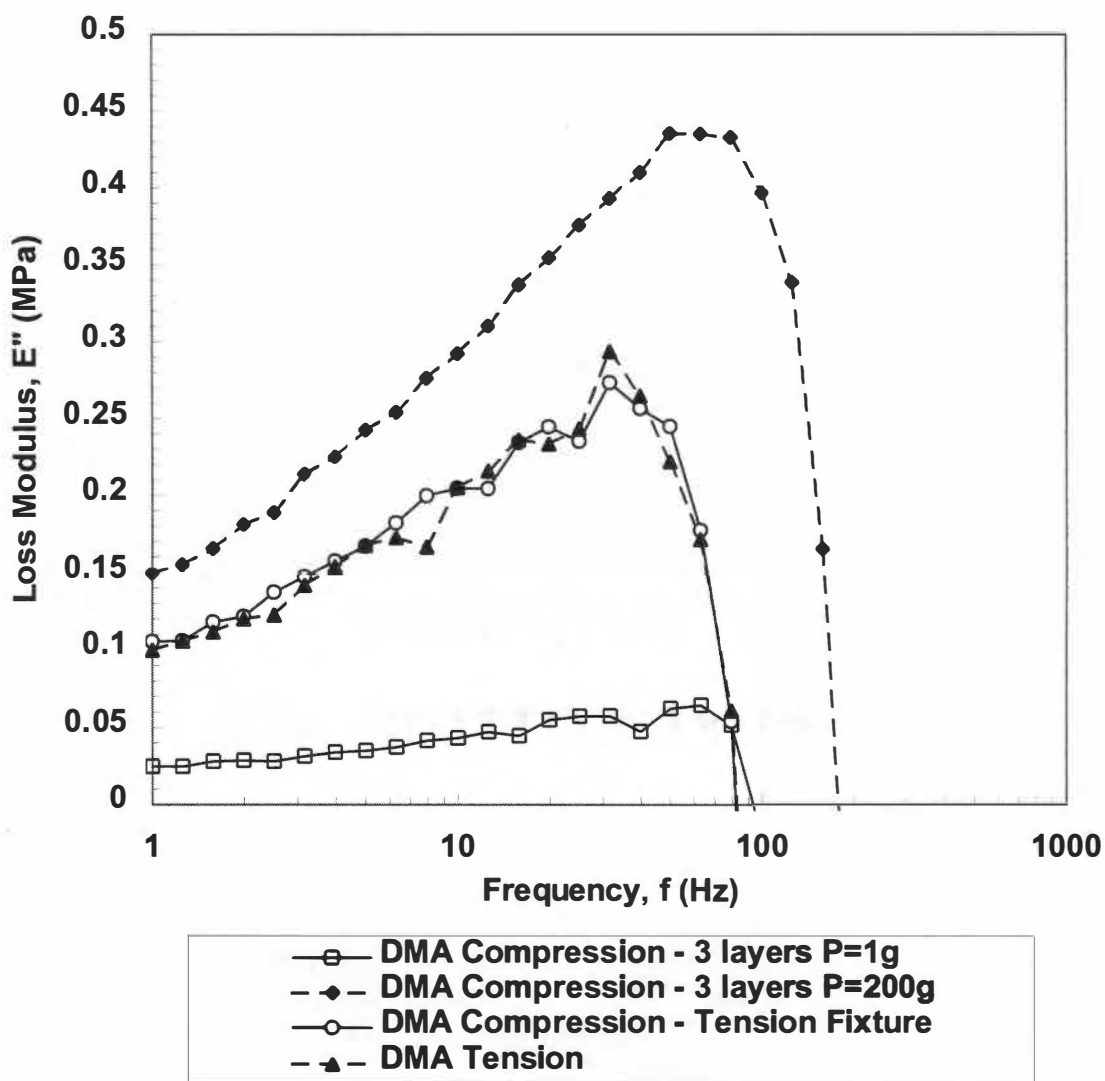


Figure 49. A plot of loss modulus versus frequency for polydimethylsiloxane using the DMA technique with a constant dynamic strain of 0.05%.

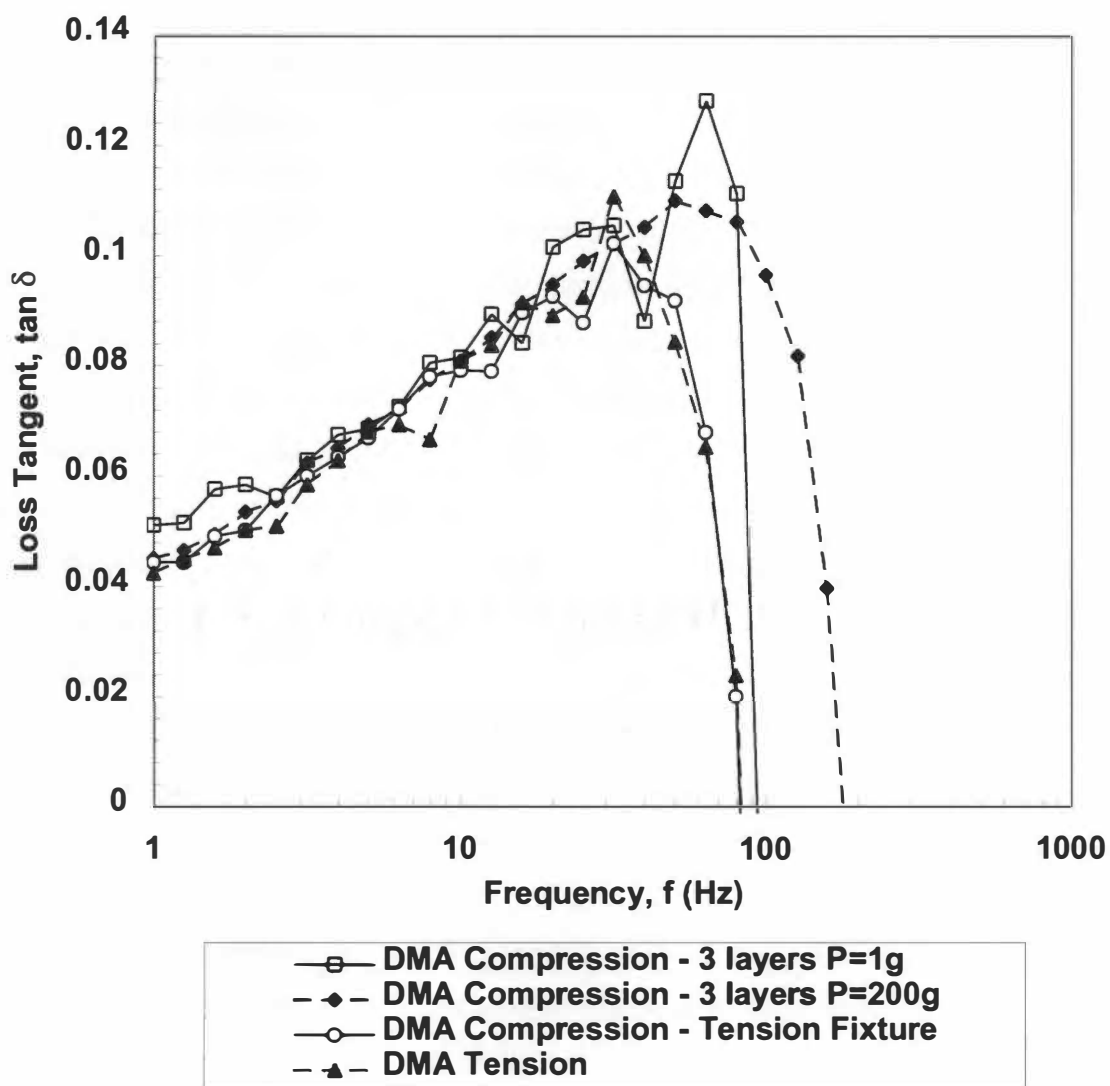


Figure 50. A plot of loss tangent versus frequency for polydimethylsiloxane using the DMA technique with a constant dynamic strain of 0.05%.

the compression fixture, only the configuration of 3 layers of material was considered for the test results shown in Figures 48 and 49 with two different static force values: 1 g (0.01N) and 200 g (2 N). In order to maintain the dynamic strain in the linear viscoelasticity region, a dynamic strain of 0.05% was used in all tests.

Figures 48 and 49 show the storage and loss moduli versus frequency for polydimethylsiloxane. As a general observation, the storage and loss moduli show approximately the same trends for all the modes and fixtures used in the test; the storage and loss moduli increase as a function of the frequency, reach a maximum, and then decrease dramatically after 40 Hz. The results for storage and loss moduli obtained using the tension fixture, i.e., in tension and compression mode, are essentially the same. However, the storage and loss moduli obtain with the compression fixture and three layers of material and a static force of 1 g are lower than with tension fixture. Furthermore, the storage and loss moduli of the polydimethylsiloxane using the compression fixture with three layers of material and a static force of 200 g are higher than the results with the tension fixture. An explanation of these effects will be given in sections 5.4.1 and 5.4.2. As noted before, measurements over 40 Hz are not accurate due to resonance of the testing apparatus. Thus, the dramatic decrease after 40 Hz does not reflect the behavior of the material.

Figure 50 shows DMA results for the loss tangent versus frequency for polydimethylsiloxane. Again, the distinct differences in the storage and loss moduli observed for each of the different deformation modes do not appear in the loss tangent. This is due to the fact that the loss tangent measurement is independent of the fixture mode and the geometry of the sample. The loss tangent initially increases as a function of the frequency and then dramatically decreases after 40 Hz. The decrease at 40 Hz is again due to the passage of a resonance in the testing apparatus and does not reflect the behavior of the

material. Results for the loss tangent are similar for all the modes and fixtures used.

5.4 COMPARISON OF INDENTATION AND DMA TESTING

Tables 1 and 2 present a summary of results for DMA tests on the polyurethane and the polydimethylsiloxane. The upper part of each table presents important results obtained using the DMTA V instrument. The lower part shows the static stress, obtained from equation (25), and the static strain, calculated by making the assumption that the elastic moduli, E , of the polyurethane and the polydimethylsiloxane are 4 MPa and 2 MPa, respectively, and using Hooke's law relating the strain and the stress as:

$$\sigma = E\varepsilon \quad (52)$$

In comparing the indentation and DMA results, it is important to note the relative static and dynamic strains. Indeed, the behavior of the material can depend on the static and dynamic strains, so a comparison of indentation and DMA results is valid only if the static and dynamic strains are about the same.

The static and dynamic strain for the indentation tests with a flat punch can be calculated from equations (17) and (19), respectively. For the polyurethane, the static strain for indentation with the flat punch was 0.24%, which is similar to the static strain for the DMA tests with the tension fixture, 0.40%. The dynamic strain for indentation with the flat punch was 0.0003%, significantly lower than the dynamic strain for the DMA tests with the tension fixture, 0.05%. For the polydimethylsiloxane, the static strain for indentation with the flat punch was 0.56%, which is similar to the static strain for DMA tests with the tension fixture, 0.69%. The dynamic strain for indentation with the flat punch

Table 1. Summary of results for DMA tests on polyurethane.

Polyurethane					
Fixture		Compression Fixture		Tension Fixture	
Deformation mode		Compression	Compression	Compression	Tension
Number of layers		2	1	1	1
Section Area	mm ²	20.29	20.29	21.84	21.84
Height or Thickness	mm	4.12	2.06	10.6	10.6
Dynamic Strain	%	0.05	0.05	0.05	0.05
Dynamic Stress	KPa	3-20	4-22	2-15	2-15
Static Force	N	4	4	0.10-0.35	0.10-0.35
Dynamic Force	mN	60-400	90-450	50-320	50-320
Dynamic Displacement	um	2	1	5	5

Static Stress	KPa	197.10	197.10	16.03	16.03
Static Strain	%	4.93	4.93	0.40	0.40

Table 2. Summary of results for DMA tests on polydimethylsiloxane.

Polydimethylsiloxane					
Fixture		Compression Fixture		Tension Fixture	
Deformation mode		Compression	Compression	Compression	Tension
Number of layers		3	3	1	1
Section Area	mm ²	17.63	17.63	7.21	7.21
Height or Thickness	mm	2.54	2.54	6	6
Dynamic Strain	%	0.05	0.05	0.05	0.05
Dynamic Stress	KPa	0.2-0.3	2	1.2	1.3
Static Force	N	0.01	2	0.1	0.1
Dynamic Force	mN	4-5	30-40	10	10
Dynamic Displacement	um	1	1	3	3

Static Stress	KPa	0.57	113.48	13.87	13.87
Static Strain	%	0.03	5.67	0.69	0.69

was 0.0006%, significantly lower than the dynamic strain for DMA tests with the tension fixture, 0.05%. However, even though the dynamic strains for the DMA tests were significantly different from indentation tests using the flat punch, they were still small enough for linear viscoelasticity, to predominate.

Inspection of the data in Tables 1 and 2 shows that the DMA results obtained with the compression fixture are different from those in the tension fixture. For polyurethane, the static strain using the compression fixture, 4.93%, is significantly higher than with tension fixture, 0.40%. The same is true of the tests for polydimethylsiloxane, where the static strain using the compression fixture was 0.03%, for a static force of 1 g, and the static strain was 5.67%, for a static force of 200 g. These are to be compared with the static strain of 0.69% for the tension fixture. Furthermore, we have seen in section 5.3 that there are significant differences in the viscoelastic properties of the two materials. The next section will address the reasons for these differences.

5.4.1 INFLUENCE OF SPECIMEN MISALIGNMENT AND SURFACE TILT

The DMA results using the compression fixture for both the polyurethane and the polydimethylsiloxane exhibit a problem caused by tilt of the specimen surface relative to the compression disks due to minor misalignment (see Figures 43 and 47). This same problem is observed for the flat punch indentation, as shown in Figure 31. The data in this figure show that a penetration of 1 μm is needed for full contact between the indenter and the material when using an 89 μm diameter punch. Since it is impossible to have perfect perpendicularity between the axis of the indenter and the surface, a certain amount of penetration is needed to develop full contact. The same phenomenon occurred during DMA testing with the compression fixture. A load of 100 to 150 g was needed on both

materials for the storage modulus to become approximately constant, as shown in Figures 43 and 47. The compression fixture test on polydimethylsiloxane with a static load of 1 g shows that the storage and loss moduli were significantly lower than the tension fixture test, as shown in Figures 48 and 49. This is because full contact is not developed at a static load of 1 g, so the true contact area is over estimated, resulting in lower storage and loss moduli. Therefore, the results of the DMA testing using the compression fixture on polydimethylsiloxane with a static load of 1 g shown in Figures 48 and 49 are not valid.

5.4.2 INFLUENCE OF THE SUBSTRATE

Another issue in DMA testing with the compression fixture is the influence of the substrate. This effect is especially important in thin film indentation testing using both the Berkovich and flat punch indenters. For example, using a flat punch, as the indenter penetrates the material, the storage modulus increases until full contact is reached, as shown in Figure 31. After remaining constant for a certain degree of penetration, it then starts to increase again due to the influence of the substrate. Put another way, when the penetration of the film becomes large in comparison to its thickness, the static strains in the film can become significant, leading to a change in the dynamic response of the film. For DMA tests using the compression fixture, the same effect can be observed. In Figures 44 and 45 for polyurethane, the tests using the compression fixture exhibit larger storage and loss moduli than the tension fixture test. This is consistent with the results presented in Table 1, where the static strain for the compression fixture, 4.93%, was significantly higher than for the tension fixture, 0.40%. The same observation can be made for polydimethylsiloxane using a static force of 200 g. Indeed, the static strain for the compression fixture, 5.67%, was significantly higher than for the tension fixture, 0.69%, yielding larger storage and loss moduli

as seen in Figures 48 and 49. Moreover, for polyurethane, the test on one layer of material shows results higher than with two layers of material. These results are all consistent with substrate influences on the measurements.

To summarize the importance of these two effects, when the indenter penetration into the film stays small in comparison to the film thickness, three different zones can be observed in the plot of the storage and loss moduli versus penetration depth, as shown in Figure 51. At shallow depths, the first zone corresponds to the rise of the moduli due to misalignment of the flat punch and the surface of the specimen. As the indenter penetrates the surface, the moduli reach a plateau corresponding to the second zone. When the indenter penetration into the film becomes large in comparison to the film thickness, the moduli increase again due to the substrate effect. When the film is not thick enough compared to the flat punch diameter, the first and third zone can merge together, making the plateau disappear, as shown in Figure 52. The same trend can be observed for DMA tests. None of the tests using the compression fixture (see Figures 43 and 47) exhibited a clear plateau, which confirms that the measurements were affected by the substrate.

5.4.3 POLYURETHANE

Because of surface tilt and substrate influences on the DMA compression tests, the measurements with the tension fixture are the most valid. Moreover, an analysis of the DMA machine response revealed that measurements at frequencies greater than 40 Hz are influenced by resonance of the testing apparatus. These observations are important in comparing the viscoelastic properties of the polymeric materials measured with indentation and DMA techniques.

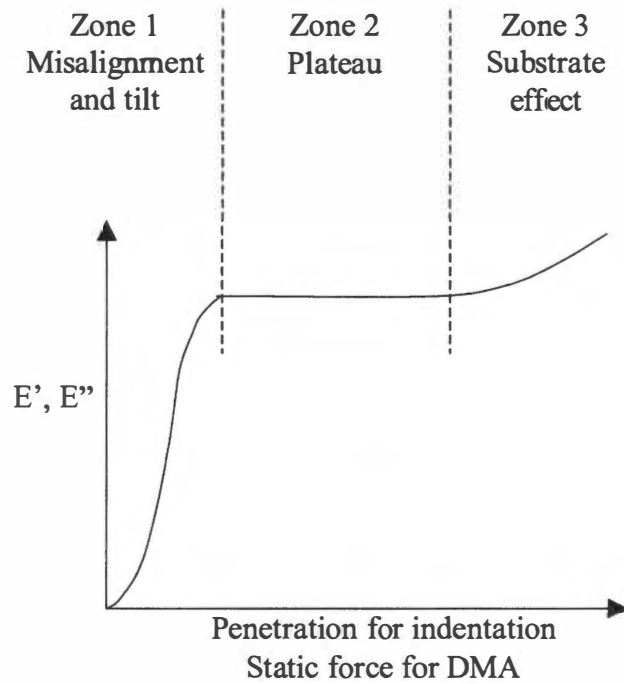


Figure 51. A schematic plot of storage and loss moduli versus penetration depth for indentation, or static force for DMA, showing the influence of misalignment, tilt, and the substrate.

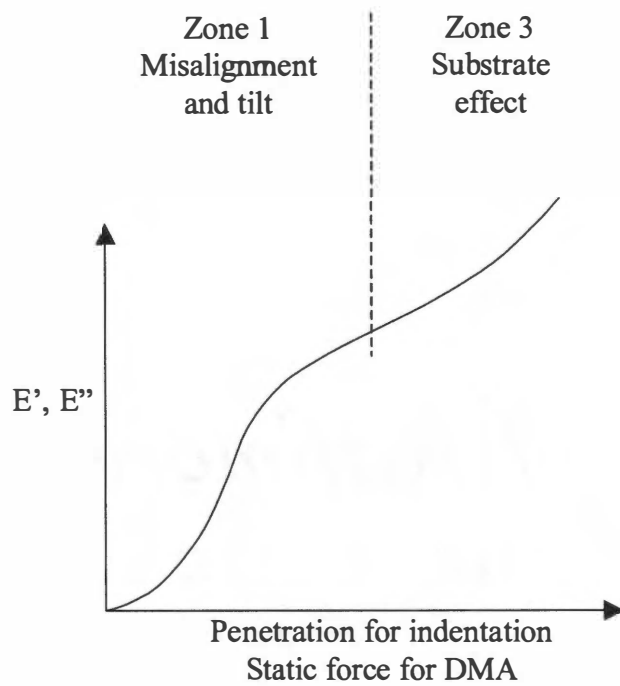


Figure 52. A schematic plot of storage and loss moduli versus penetration depth for indentation, or static force for DMA, showing the disappearance of the plateau when the punch diameter is larger in comparison to the specimen thickness.

Figures 53 and 54 show plots of storage and loss moduli, respectively, versus frequency for polyurethane using both indentation and DMA techniques. The same behaviors and trends are observed for all the tests. Nevertheless, the storage and loss moduli at frequencies less than 40 Hz from the indentation tests, using both the Berkovich and flat punch indenters, are slightly higher than the DMA tests using the tension fixture.

Figure 55 shows a plot of loss tangent versus frequency for polyurethane using both indentation and DMA techniques. Again, the same trends and behaviors are observed for all the tests. Nevertheless, the loss tangent for frequencies less than 40 Hz from the indentation tests, using both Berkovich and flat punch indenters, are slightly higher than the DMA test using the tension fixture.

Although the trends of the viscoelastic properties for polyurethane are the same for indentation and DMA tests, there are a small number of outliers in the data that produced a factor of two difference for polyurethane. Nevertheless, the storage moduli values are in good accordance with the tensile modulus from the literature [18].

5.4.4 POLYDIMETHYLSILOXANE

Figure 56 shows a plot of storage modulus versus frequency for polydimethylsiloxane using both indentation and DMA techniques. The same general behavior is observed for all the tests. The storage moduli for frequencies less than 40 Hz from the indentation tests, using both the Berkovich and flat punch indenters, are slightly lower than the DMA test using the tension fixture, but generally in good agreement.

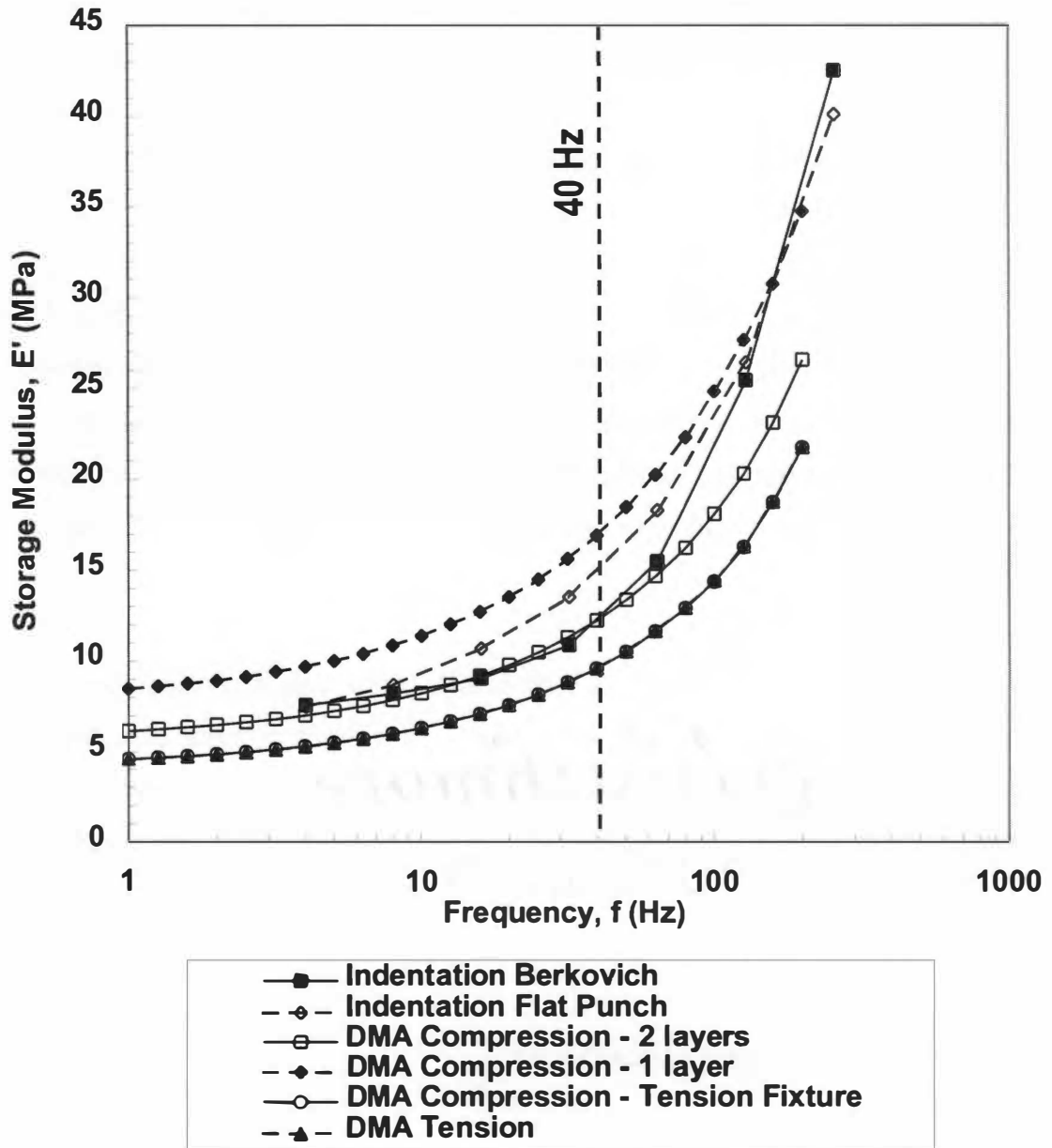


Figure 53. A plot of storage modulus versus frequency for polyurethane using indentation and DMA techniques. The indentations tests were performed with both Berkovich and flat punch indenters. The DMA tests were performed at a constant dynamic strain of 0.05%.

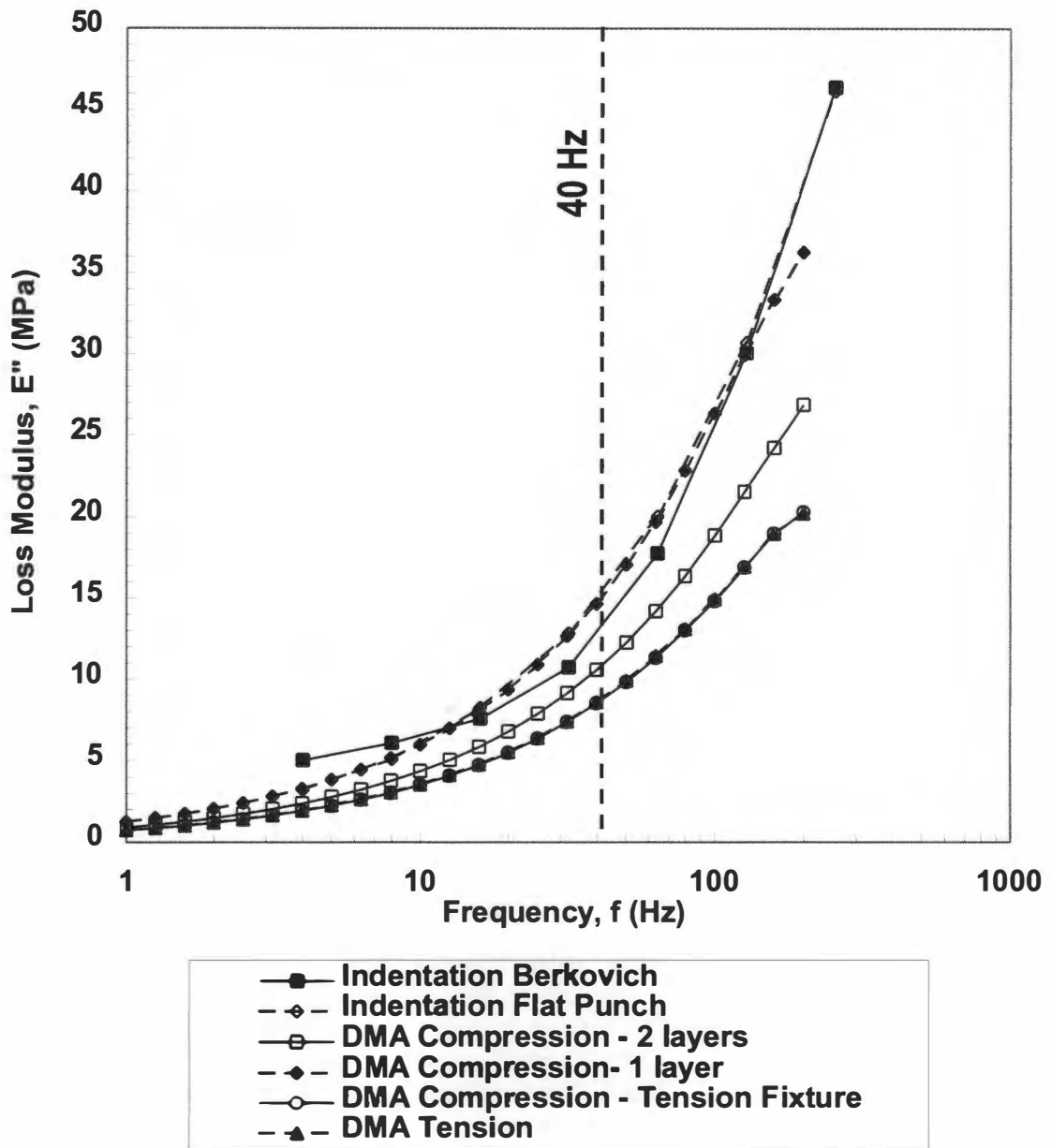


Figure 54. A plot of loss modulus versus frequency for polyurethane using indentation and DMA techniques. The indentations tests were performed with both Berkovich and flat punch indenters. The DMA tests were performed at a constant dynamic strain of 0.05%.

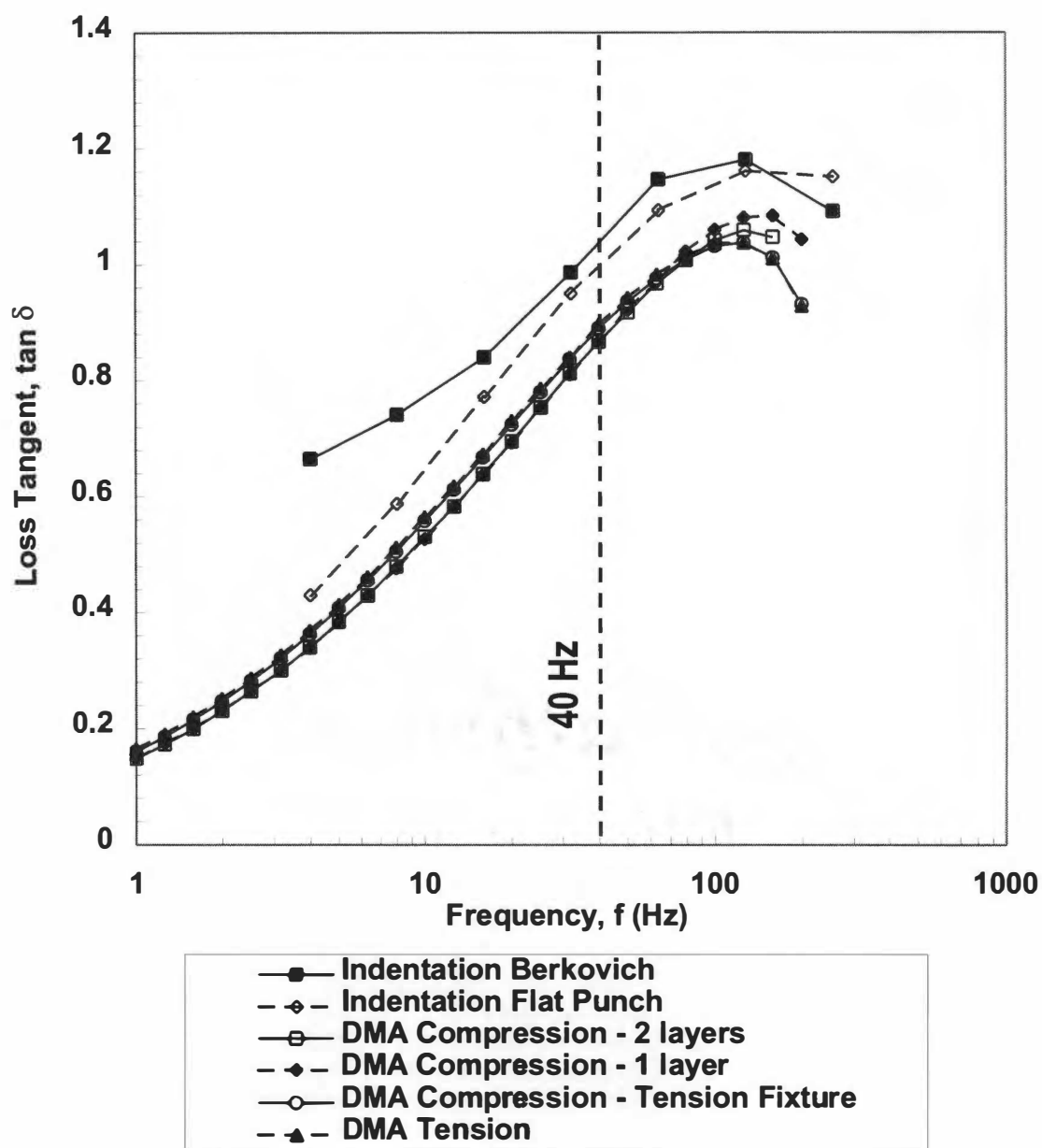


Figure 55. A plot of loss tangent versus frequency for polyurethane using indentation and DMA techniques. The indentations tests were performed with both Berkovich and flat punch indenters. The DMA tests were performed at a constant dynamic strain of 0.05%.

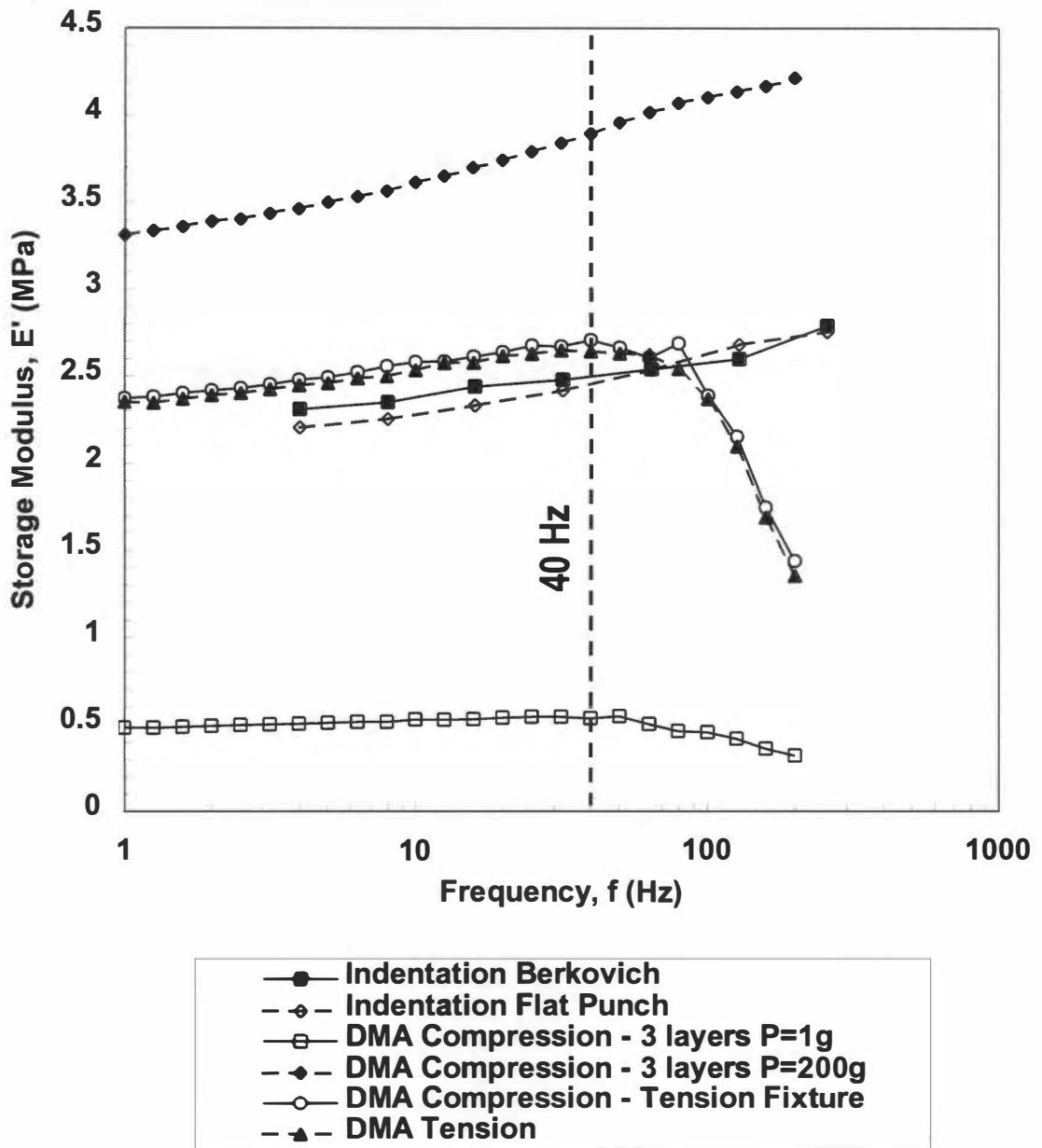


Figure 56. A plot of storage modulus versus frequency for polydimethylsiloxane using indentation and DMA techniques. The indentations tests were performed with both Berkovich and flat punch indenters. The DMA tests were performed at a constant dynamic strain of 0.05%.

Figures 57 and 58 show plots of the loss modulus and loss tangent versus frequency for polydimethylsiloxane using both indentation and DMA techniques. Again, the same general behavior is observed for all the tests. The loss modulus and the loss tangent for frequencies less than 40 Hz from the indentation tests, using both the Berkovich and flat punch indenters, are similar to the DMA tests using the tension fixture.

Although the trends of the viscoelastic properties for polydimethylsiloxane are the same for indentation and DMA tests, there are a small number of outliers in the data that produced a difference of 20%.

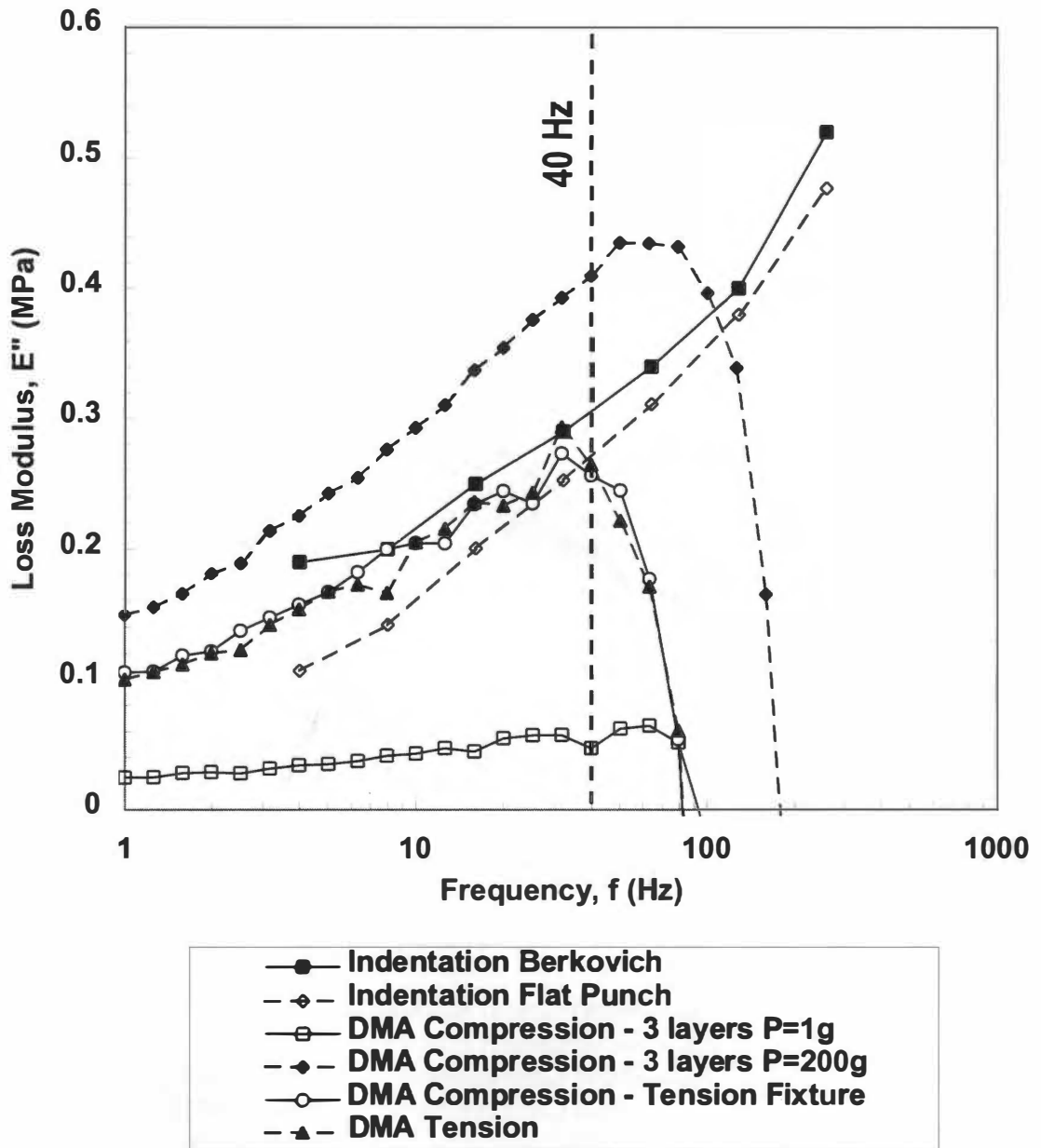


Figure 57. A plot of loss modulus versus frequency for polydimethylsiloxane using indentation and DMA techniques. The indentations tests were performed with both Berkovich and flat punch indenters. The DMA tests were performed at a constant dynamic strain of 0.05%.

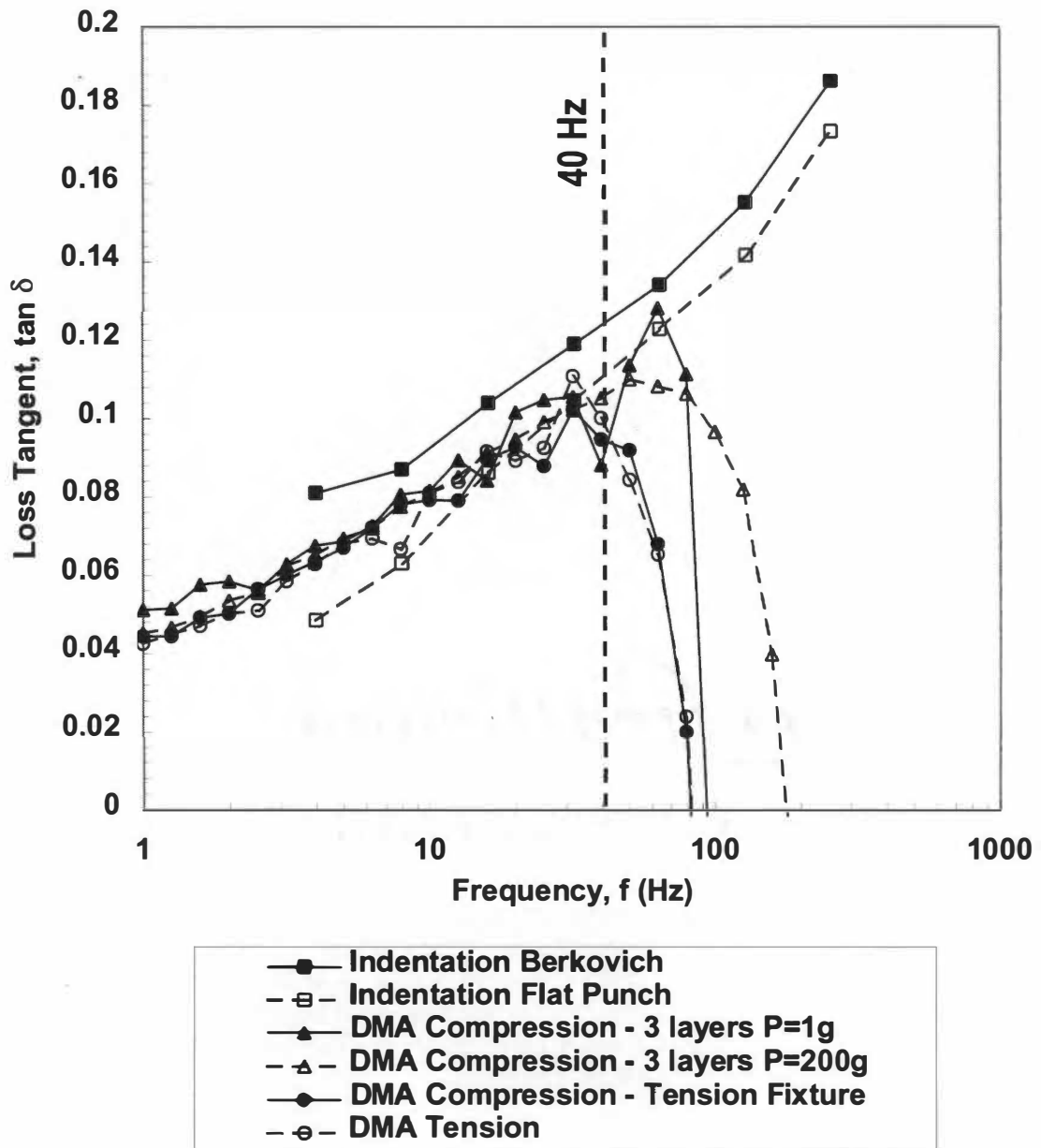


Figure 58. A plot of loss tangent versus frequency for polydimethylsiloxane using indentation and DMA techniques. The indentations tests were performed with both Berkovich and flat punch indenters. The DMA tests were performed at a constant dynamic strain of 0.05%.

CHAPTER 6 CONCLUSIONS

Using a depth-sensing indentation system in a frequency-specific measurement mode, the viscoelastic properties of polymeric materials can be measured at various frequencies.

A new automated test methodology has been developed to measure the viscoelastic properties of very soft polymeric material at various frequencies using frequency-specific DSI. This new methodology is based on improvements of the measurement accuracy and precision of the frequency-specific DSI technique, and improved instrument calibrations over the frequency range. As a consequence, the useful frequency range of the Nano Indenter[®] DCM has been increased from 5 to 250 Hz, with the ability to measure stiffnesses as low as 5 N/m. Furthermore, the test methodology has been developed to work with two different indenter tip geometries: a Berkovich pyramid and circular flat punch.

The new measurement technique has been used to compare the viscoelastic properties of two polymeric materials, a polyurethane (PU) and a polydimethylsiloxane (PDMS), using the two different tip geometries (Berkovich and flat punch). Indentation tests with the Berkovich and flat punch indenters give similar results over the range of frequency, provided the area of contact are the same.

The two polymeric materials have also been tested with a bulk dynamic mechanical testing technique, Dynamic Mechanical Analysis (DMA). In comparing the majority of the indentation and DMA results, both techniques clearly illustrate the same trends, provided the static and dynamic strains are comparable. However, there were a small number of outliers in the data that produced a difference of 20% for polydimethylsiloxane and a factor of two difference for polyurethane.

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VITA

Nicolas Conte was born December 24, 1972 in Nantes, France. He attended intermediate in the Jules Verne Public School in Nantes and High School in the Livet Public Technological School in Nantes, where he graduated in June of 1992. He attended the University of Nantes for three years where he studied Physics, Math, and Technology. He received his Diplome d'Etudes Universitaires Generales in June 1995. He attended the University of Nantes (associated with the Ecole Centrale Nantes) for one year and received his Licence de Technologie Mecanique in June 1996. He enrolled in the French Navy for one year to do his military service. Then, he attended the University of Nantes (associated with the Ecole Centrale Nantes) for one year and received his Maîtrise de Technologie Mecanique (US equivalent: Bachelor's degree in Mechanical Technology) in June 1998. Upon graduation, he entered the National Engineer School of Saint-Etienne (ENISE) in France, where he studied engineering, mechanics, and management. While enrolled at ENISE, he came for a five months internship at MTS Nano Instrument Innovation Center, Oak Ridge, Tennessee. He received his Mechanical Engineer Diploma from ENISE and graduated valedictorian in June 2000. He entered graduate school at the University of Tennessee, Knoxville, in the Materials Science and Engineering program. In June 2001, while enrolled at the University of Tennessee, he became employed at MTS Nano Instrument Innovation Center as an application engineer. His Master of Science degree was conferred in May of 2002.