Instrument-independent dynamic mechanical analysis of polymeric systems

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Large discrepancies are often observed among data obtained by different dynamic mechanical instruments, different analysis methods, or even different laboratories using identical instruments. Four commonly used dynamic mechanical instruments, the Rheovibron, the DMA 982 and 983, the Dynastat, and the PPM-R5 sonic tester, were methodically analysed for type of deformation as well as frequency–temperature relationships that may affect comparison of their data. Such discrepancies were shown to arise from the instruments' limited ranges of test frequencies, types of deformation, types of material tested, and the material morphology, orientation and conformation as well as limitations of theoretical methods of analysis and overall test sensitivity to external factors. Through the use of macro- and microscopic theory of elasticity as well as the time–temperature superposition principle, along with careful experimental set-ups, the dynamic mechanical responses of a set of well characterized polyethylene samples were successfully compared with one another across all instruments.

(Keywords: dynamic mechanical analysis; instrumentation; polyethylene; orientation; crystallinity)

INTRODUCTION

Measurements of material response to oscillations imposed by mechanical load or deformation provide insight into various aspects of material structure. They are especially responsive to various molecular motions that manifest themselves at various temperatures, and may influence such properties as fatigue and impact resistance[1–3]. Even though the principles of dynamic testing are well established, large discrepancies are often observed among data obtained by different instruments, different analysis methods, or even different laboratories using identical instruments. Such discrepancies may arise from the instruments' limited ranges of test frequencies, types of deformation, types of material tested, and the material morphology, orientation and conformation as well as limitations of theoretical methods of data analysis and overall test sensitivity to external influences[1].

In this work, the dynamic mechanical responses of a set of well characterized polyethylene films[4–9] were examined by various dynamic mechanical instruments. In doing so, insight was gained into the dynamic mechanical behaviour of the polyethylene samples while the polymer itself was analysed on an instrument-independent basis. The Rheovibron, the Dynastat, the DuPont DMA 982 and 983, and the Sonic Pulse Propagation Meter PPM-5R were employed in this study. The operating conditions of these instruments are summarized in *Table 1*. The Dynastat and the DMA 983 can perform other viscoelastic experiments such as creep and stress relaxation. To compare results of properly formulated experiments among these dynamic mechanical instruments, the relationships among various operating parameters are to be established. For instance, how do experiments performed at different amplitudes compare with one another? How does an experiment performed on the DMA at changing resonant frequencies compare with experiments on the Rheovibron at a fixed frequency? How would two experiments on the Rheovibron and the Dynastat compare with one another under similar operating conditions? These and similar questions were answered based on mechanical analysis of the methods of instrument operation as well as the principles of viscoelasticity.

PRINCIPLES OF DYNAMIC MECHANICAL ANALYSIS

The dynamic mechanical properties of polymeric materials are analysed by imposing a sinusoidal stress σ^* or strain ε^* as input on a polymer sample and recording its corresponding response, viz.:

$$\text{input:} \sigma^* = \sigma_0 e^{i\omega t} \qquad \text{response: } \varepsilon^* = \varepsilon_0 e^{i\omega t - \delta} \quad (1)$$

or

$$\text{input:} \varepsilon^* = \varepsilon_0 e^{i\omega t} \qquad \text{response: } \sigma^* = \sigma_0 e^{i\omega t + \delta} \quad (2)$$

where σ_0 and ε_0 are the amplitudes of respective stress and strain cycles; ω is the angular frequency (related to vibrational frequency f as $\omega = 2\pi f$); and δ is the phase lag between stress and strain, and is attributed to the viscoelastic nature of the material. If stress and strain are so measured, the sample dynamic complex modulus M^* or compliance S^* are determined as:

$$M^* = M' + iM'' \qquad S^* = S' - iS'' \quad (3)$$

$$M' = |M^*| \cos \delta \qquad S' = |S^*| \cos \delta \quad (4)$$

$$M'' = |M^*| \sin \delta \qquad S'' = |S^*| \sin \delta \quad (5)$$

$$\tan \delta = M''/M' \qquad \tan \delta = S''/S' \quad (6)$$

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Table 1 Description of basic operating parameters of the Rheovibron, DMA 982/983, Dynastat and PPM-5R sonic tester

Instrument	Sinusoidal input	Output	Amplitude[a] (mm)	Frequency[a] (Hz)
Rheovibron	Strain	Stress	16×10^{-4} to 160×10^{-4}	3.5, 11, 35, 110, fixed
DMA 982	Strain	Damping and frequency	0.05 to 2, fixed	≈ 10 to ≈ 50, resonant
DMA 983	Strain or stress	Damping and stress or strain	0.05 to 2, fixed	≈ 0.01 to ≈ 10, fixed; and ≈ 10 to ≈ 50, resonant
Dynastat	Stress or strain	Strain or stress	0.0005 to 5 mm, 0.01 to 10 kg, variable	0.01 to 99.99, fixed
Sonic PPM-5R	Strain	Transmit time	Micrometre range, fixed	5000, fixed

[a] Fixed: measurements are made at a fixed frequency or amplitude
Variable: measurements are made over a range of frequencies or amplitudes

$$M' = S'/(S'^2 + S''^2) \qquad S' = M'/(M'^2 + M''^2) \qquad (7)$$

$$M'' = S''/(S'^2 + S''^2) \qquad S'' = M''/(M'^2 + M''^2) \qquad (8)$$

where M' and S' are the storage modulus and compliance and M'' and S'' are the loss modulus and compliance, respectively. The stress–strain phase lag is δ. Compliance has been known to relate more easily to polymer structure and would thus be used in place of moduli throughout this work[2].

EXPERIMENTAL

The dynamic mechanical results of well characterized, unoriented and uniaxially oriented polyethylene films were examined. The morphology, orientation and chain conformation of these films have been studied extensively by X-ray diffraction[8], refractive index[5,8], birefringence[5,8] and infra-red dichroism spectroscopy[6] and were related to the dynamic mechanical data of the Rheovibron[4,9] by Seferis and Wedgewood. *Table 2* contains some of the characterization results such as volume fraction crystallinity, Hermans' orientation function (f) and the fourth moment of the orientation distribution (g) of the polyethylene samples of this study[8]. The polymer was modelled as a two-phase system comprised of crystalline and non-crystalline phases. Strips were cut from the available polyethylene films. For oriented samples, the strips were cut at various angles required by the experiment from the draw direction as shown in *Figure 1*.

Dynamic mechanical analysis similar to the present study was performed on the Rheovibron by Wedgewood and Seferis[4]. Their analysis and modifications allowed for reproducibility of 5% on the Rheovibron. Thus in this study, Rheovibron data[8,9] were used as the accurate base standard for comparison of data with other instruments. In doing so, instrument parameters were adjusted and set to duplicate closely the Rheovibron whenever possible. In all of the experiments, deformation amplitudes were set well within the linear viscoelastic limit of the polymer. The deformation rates among various instruments were also comparable. In all the experiments, care was taken to ensure good clamping; provide good sample alignment in order to minimize sample slippage; improve the purge system in order to reduce condensation and freeze-up at subzero temperatures; and add electronic equipment for extended monitoring of the instrument balance, calibration and measurement[4]. Specific instruments and sample set-ups are detailed in the following sections.

Table 2 Volume fraction crystallinity (V_c), Hermans' orientation function (f) and second moment of orientation distribution (g) for the polyethylene samples used for this study

Unoriented films		Oriented films	
HU3	$V_c = 0.550$	H1	$V_c = 0.630$ $f_c = 0.63$ $g_c = 0.50$ $f_a = 0.17$ $g_a = 0.19$
HU4	$V_c = 0.625$		
HU10	$V_c = = 0.716$		

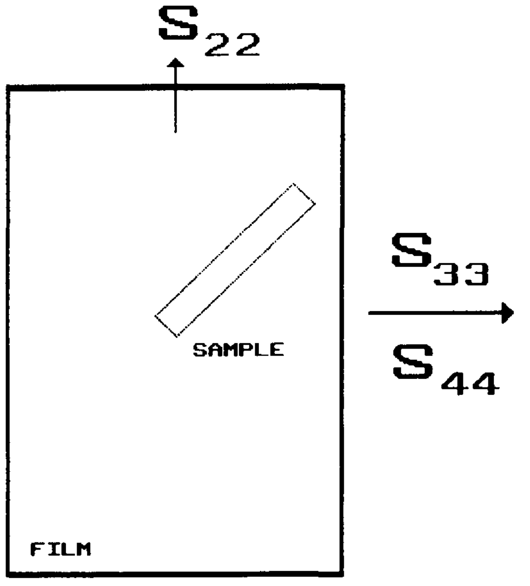

Figure 1 Schematic of film strips cut at various angles from the draw direction. S_{22}, S_{33} and S_{44} are the transverse direction tensile, draw direction tensile and shear compliance, respectively

Rheovibron Dynamic Viscoelastometer

Rheovibron measurements were done in extension[4,8–10]. A polyethylene film strip sample was mounted and properly aligned within the Rheovibron sample holder[4]. To prevent the samples from buckling, a static strain greater than the oscillating strain was simultaneously imposed on the sample. Experiments were done under dynamic displacement at a frequency of 11 Hz. To reflect the true dynamic mechanical properties of the material, the sample's properties were extrapolated to a stress-free state so that their dependence was only on temperature and frequency[4]. Care was also taken to account for the uniformity of the imposed stress, effects of the non-linear stress–strain behaviour of the material, and the effect of the compliance of various parts of the instrument[4].

DuPont Dynamic Mechanical Analyzer DMA 982 and DMA 983

The DuPont DMA 982 and 983 measurements were done in flexure. The DMA was used with the DuPont 1090 and 9900 Thermal Analysis Controller Systems. A polyethylene strip was aligned and clamped in the DMA's horizontal clamps, perpendicular to the DMA's parallel arms under a small amount of torque. The experiments were done at the sample's resonance frequency. The DMA 982 operated at a constant amplitude of 0.05 mm, equivalent to a strain of 0.25%. This strain was well below the linear elastic limit of the polymer. The set of equations describing the dynamics of the DMA[11,12] was programmed in FORTRAN on a VAX 11/750 computer and was used for parametric studies of the model, independent of the software supplied with the instrument. In order to analyse the dynamic mechanical data of the polyethylene samples on a quantitative basis, the contributions from various modes of deformation in the DMA as well as the effect of the changing resonance frequency during the course of the thermal scan on the final dynamic mechanical results were addressed and are detailed in the theoretical section. To verify experimentally the theoretical fixed frequency reductions of the DMA 982 resonant data, identical experiments were performed on the DMA 983 at a fixed frequency of 10 Hz while the data were analysed by the software provided by the manufacturer.

Dynastat

The Dynastat was operated in its dynamic displacement mode. A polyethylene strip sample was mounted and aligned between two clamp assemblies designed for testing of samples in tension similar to an earlier design on the Rheovibron that proved successful[4]. Without any sample present, the Dynastat gain settings were first set to zero. Then, Gain 1, Gain 2, Damping, Rise Time, Compensation 1 and Compensation 2 gains were adjusted for stable electronic operation by minimizing the gain settings through minimization of instrument noise displayed in the stress and strain signals as monitored by an oscilloscope. The amplitude of deformation was set to 7%, a value within the linear viscoelastic limit of these polyethylene films. The sample was scanned from 1 to 99.9 Hz at five equally spaced frequencies per decade. Data reported were averaged over 15 cycles per measurement in order to increase signal-to-noise ratio[13].

Sonic Pulse Propagation Meter PPM-5R

The sonic tester was set up to produce tensile as well as shear waves and thus measure the tensile and shear compliances of the polyethylene films. The sonic tester transmits waves every 5 ms at 5 kHz for approximately 10^{-5} s. The pulse repetition rate was small enough to allow each mechanical pulse to dampen out before the next pulse was propagated. The sonic experiments were all performed at room temperature. For the sonic tester, the amplitude of deformation was in the micrometre level[14]. This strain is within the linear elastic limit of the polyethylenes tested.

Having detailed the set-up of each instrument employed in acquiring the dynamic mechanical properties of the polyethylene samples, a discussion of the theoretical foundation required to analyse data from various instruments follows.

THEORETICAL

Analysis of the dynamic mechanical data of various instruments requires that the relationship between time (frequency) and temperature as well as the identification of various modes of deformation and the elastic constants associated with them be addressed for each instrument. Based on the principles of viscoelastic analysis as well as macro- and micromechanical elasticity theory, a methodology for analysis of experimental data of this study was developed.

Phase separation and time–temperature analysis

Dynamic mechanical experiments, in this study and in general, are commonly performed under either resonant or forced frequencies while the temperature is being scanned and the stress–strain behaviour of the material is being recorded. For the fixed, forced frequency case of the Rheovibron and the Dynastat, the dynamic mechanical response is investigated at constant frequency f while the temperature is changing. For the resonant frequency case as in the DMA 982, both temperature and frequency changes throughout the experiment are shown in *Figure 2* for a representative case. To compare fixed and variable frequency results, time and temperature need to be related to one another. The time–temperature correspondence can be demonstrated either by assuming that the material behaves according to a model viscoelastic response such as a linear elastic solid[15], or by using a relationship that demonstrates the time and temperature correspondence. Time–temperature superposition may be done according to free volume models such as that of Williams–Landel–Ferry (WLF)[16], or by approximating the viscoelastic response by some function such as relaxation or retardation function[17], or by energy activated models[18]. The WLF approach was employed in this study.

According to the WLF time–temperature superposition, the compliance S of a polymer measured at temperature T_1 and frequency f_1 can be related to the compliance of that polymer at some other temperature T_2 by a frequency shift factor a_{12} defined by the WLF equation as:

$$S(T_1, f_1) = S(T_2, a_{12} f_1) \qquad (9)$$

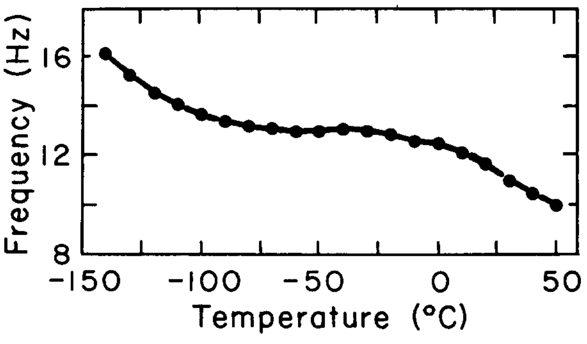

Figure 2 The change in resonant frequency as a function of temperature for the unoriented HU4 polyethylene films measured by the DMA 982

where

$$\log a_{12} = \frac{-C_1(T_2 - T_1)}{C_2 + (T_2 - T_1)} \tag{10}$$

C_1 and C_2 are constants. WLF superposition is only applicable to amorphous polymers above their T_g. However, the polyethylene samples of this study are semicrystalline. In order to satisfy this requirement of the WLF time–temperature superposition, the two-phase model was used to separate the crystalline and non-crystalline phase contributions to the bulk compliance of the polyethylene films as previously demonstrated by Seferis, Elia and Wedgewood[7]. For an unoriented sample, the two-phase separation can be done as:

$$S = A_c V_c + A_a V_a + \Phi_{a-c} \tag{11}$$

where A_c and A_a are the compliances of the crystalline and non-crystalline phases, and V_c and V_a their respective volume fractions. A plot of the bulk compliance *versus* crystallinity of samples of several different volume fraction crystallinities provided A_c and A_a for our work. The term Φ_{a-c} is the form factor term accounting for the non-ideality of the two-phase separation and has been proven to be negligible for these polyethylene samples[8,9]. It is reasonable to assume that the crystalline phase behaves in an elastic fashion and thus the viscoelastic time-dependent response of the material is dominated by its non-crystalline component:

$$S(T_1, f_1) = A_c V_c + A_a(T_1, f_1) V_a \tag{12}$$

Time–temperature superposition was thus performed on the non-crystalline phase compliance:

$$A_a(T_1, f_1) = A_a(T_2, a_{12} f_1) \tag{13}$$

The superposed non-crystalline phase compliance was then recombined with the crystalline phase compliance to give the time–temperature shifted bulk compliance. This can be demonstrated mathematically in the following manner:

$$S(T_2, a_{12} f_1) = A_c V_c + A_a(T_2, a_{12} f_1) V_a \tag{14}$$

To convert variable frequency data to constant frequency data, temperature T_1, at which the frequency of the experiment was f_1, was taken as a reference temperature. The frequency of all points on the thermogram was shifted to f_1, producing an isofrequency thermogram. Sample compliances were thus shifted with respect to time and temperature according to the superposition, generating a series of isofrequency thermograms. This is graphically shown in *Figure 3*. A similar methodology by Chartoff on amorphous polymers has proved the feasibility of this approach[19]. This family of isofrequency thermograms was then used to extract constant frequency data from the results of variable frequency experiments.

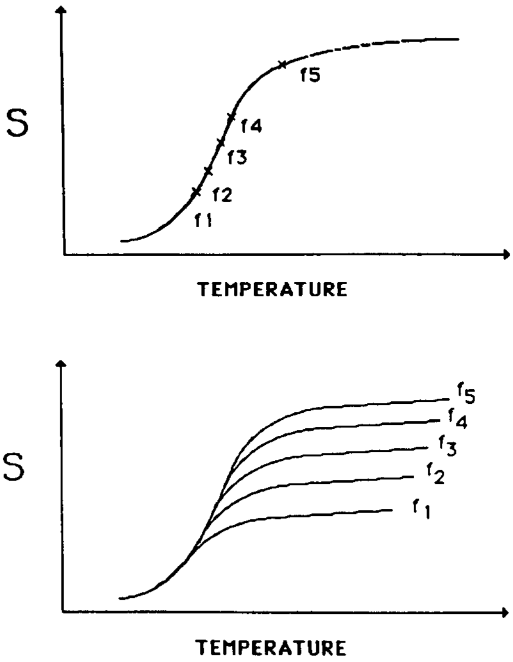

Figure 3 The methodology for superposing isofrequency and variable frequency compliance data

Mode-of-deformation analysis

Many instruments perform mechanical analysis under extension, shear, flexure and torsion modes of deformation. The classical relationship among sample properties, sample geometry and the mode of deformation can be found in many texts[11]. If all elements of analysis are properly addressed, all tensile data must be in agreement regardless of the test instrument. Classical elasticity shows that shear data must relate to tensile data through the Poisson's ratio ν as[20]:

$$M = 2(1+\nu)G \tag{15}$$

If tensile results such as that of the Rheovibron are available with great accuracy, the results of other instruments can be checked against that of the Rheovibron. If the results are in agreement, it can be concluded that the mode of deformation is tensile. If the results differ by a factor of $2(1+\nu)$, then the mode of deformation is shear.

Such mode-of-deformation analysis can be further validated by testing of anisotropic samples. Macroscopic analysis of the stress–strain relationship in a uniaxial solid for the in-plane tensile and in-plane shear compliance, S_{33} and S_{44}, respectively, shows that[2,8,9]:

$$S_{33}(\theta) = S_{33}\cos^4\theta + S_{22}\sin^4\theta + (2S_{23} + S_{44})\sin^2\theta\cos^2\theta \tag{16}$$

$$S_{44}(\theta) = S_{44} + 4(S_{33} + S_{22} - S_{44} - S_{22}) \times (\cos^2\theta - \cos^4\theta) \tag{17}$$

where θ is the angle from the principal axis or the draw direction. An experiment along the principal axis, where $\theta = 0°$, yields a compliance value which, depending on the mode of deformation, may be either tensile S_{33} or shear S_{44}. The specific mode may be determined with an experiment in transverse direction ($\theta = 90°$). If the mode of deformation is tensile, equation (16) governs the experiment and the compliance measured by the latter experiment would be S_{22}, the transverse tensile compliance, and thus different from the draw direction compliance S_{33}. If the mode of deformation is shear, the experiment is governed by equation (17) and the transverse compliance has to be shear, S_{44}, the same as that of the draw direction experiment. In this way, one can determine the mode of deformation by comparison of the compliance measured in the draw and transverse directions of a uniaxial sample.

The mode of deformation can also be determined on a microscopic basis in terms of the constitutive crystalline and non-crystalline phase properties and their orientation distribution. In the case of uniform distribution of stress, the bulk compliance S_{ij} is given by[2]:

$$S_{ij} = \langle S_{ij} \rangle_c V_c + \langle S_{ij} \rangle_a V_a + \Phi_{a-c} \qquad (18)$$

where $\langle S_{ij} \rangle_c$ and $\langle S_{ij} \rangle_a$ are the aggregate crystalline and non-crystalline phase compliances computed by orientation averaging the structural element of each phase under uniform distribution of stress.. The form factor Φ_{a-c} was proven to be negligible for these polyethylenes[8,9]. For the bulk in-plane tensile compliance S_{33} and bulk in-plane shear compliance S_{44}, the average phase properties are[2]:

$$\langle S_{33} \rangle_p = A_p + B_p f_p + C_p f_p \qquad (19)$$

$$\langle S_{44} \rangle_p = A_{Gp} - \tfrac{1}{2}(4B_{gp} - B_p - 5C_p) f_p - 2C_p g_p \qquad (20)$$

where p can be crystalline (c) or non-crystalline (a). A_p, A_{Gp}, B_p and C_p are linear combinations of compliance constants of phase p and are intrinsic to that phase. A_p and A_{Gp} simply represent the unoriented tensile and shear compliances of phase p. The term f_p is the Hermans' orientation function and g_p is the fourth moment of the orientation distribution[2]. If the mode of deformation is shear, equation (19) is the governing equation. For an unoriented sample, f_c, f_a, g_c, g_a are all zero and the above equation will reduce to the two-phase formulation of equation (6). In the previous section, macroscopic analysis showed that, under shear deformation, a uniaxially oriented solid will exhibit its shear compliance S_{44} along the draw and transverse directions. According to the microscopic analysis of this section, the compliance of an unoriented sample of similar volume fraction crystallinity would be the same as the compliance in the draw and transverse directions of a uniaxially oriented sample, only if the mode of deformation is shear. These relationships will later be used in the determination of the mode of deformation of various dynamical mechanical instruments of this study.

The time–temperature principle as well as the interpretations of macro- and micromechanical theory of elasticity aids the analysis of both the dynamic mechanical instruments as well as the polyethylene samples. The results of this analysis are detailed in the following section.

RESULTS AND DISCUSSION

The storage and loss compliances of the unoriented HU4 polyethylene films and oriented H1 polyethylene films in the draw direction as measured by the Rheovibron are shown in *Figures 4* and *5*, respectively. The dynamic compliance of the unoriented HU4 polyethylene sample, as measured by the DMA, is shown in *Figure 6*. Also, tan δ, the ratio of loss to storage moduli or compliances, is shown in *Figure 7*. The DMA data points are plotted at 5°C intervals. The storage and loss compliances of the uniaxial H1 polyethylene samples in the draw and the transverse directions measured by the DMA 982 are shown in *Figure 8*. There has been evidence of a low-temperature transition at -60 to -40°C in polyethylene[8,9]. All our data showed such a transition. DMA data seemed to be especially sensitive to this transition compared to the Rheovibron data. The change in the resonant frequency of operation of the DMA 982 as a function of temperature for unoriented polyethylene films is shown in *Figure 2*. To compare the effect of this change in frequency on the dynamic mechanical data of DMA compared to that of the Rheovibron, time–temperature as well as mode-of-deformation analysis was performed.

Phase separation and time–temperature analysis

The effects of resonant frequency change of DMA on the dynamic compliance results were analysed using the

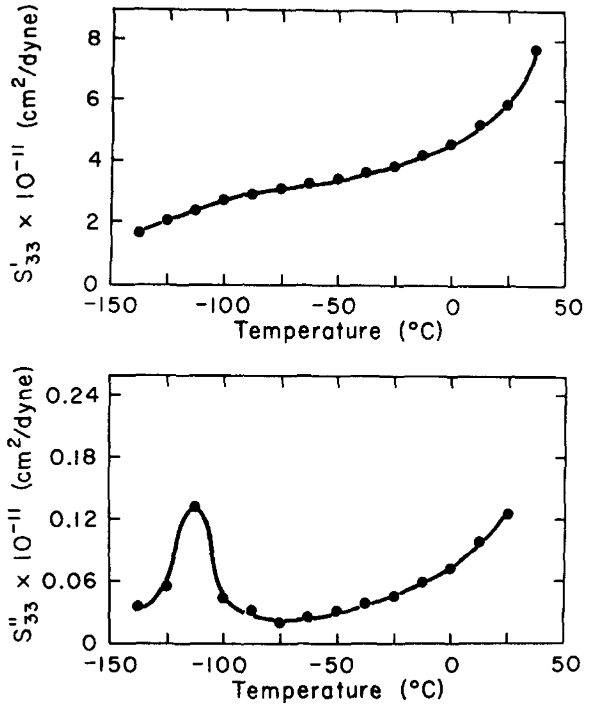

Figure 4 The storage and loss compliances of the unoriented HU4 polyethylene films measured by the Rheovibron

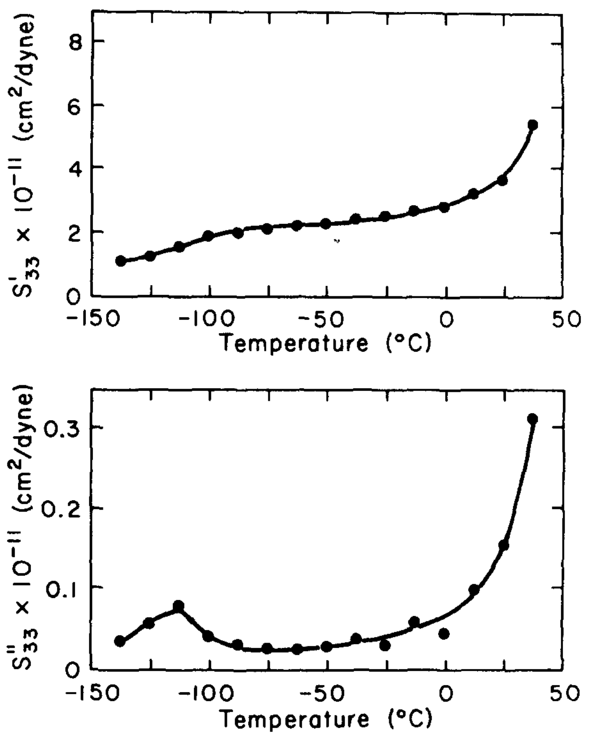

Figure 5 The storage and loss compliances of the oriented H1 polyethylene films along the draw direction measured by the Rheovibron

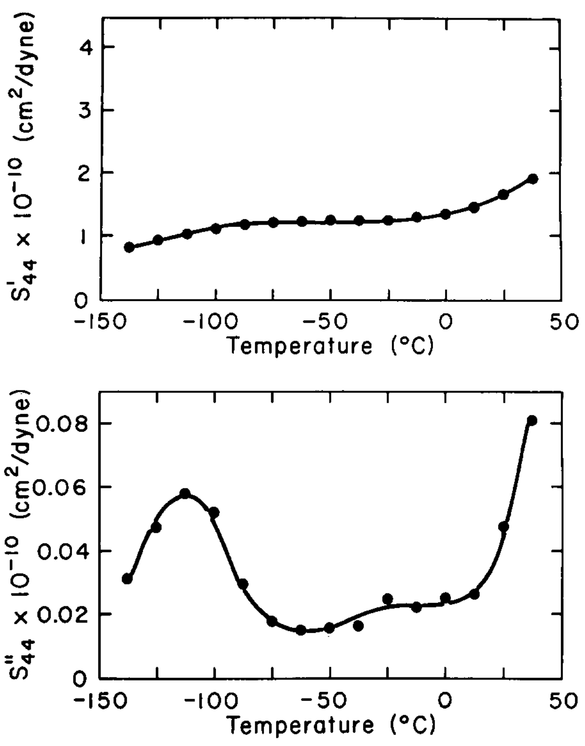

Figure 6 The storage and loss compliances of the unoriented HU4 polyethylene films measured by the DMA 982

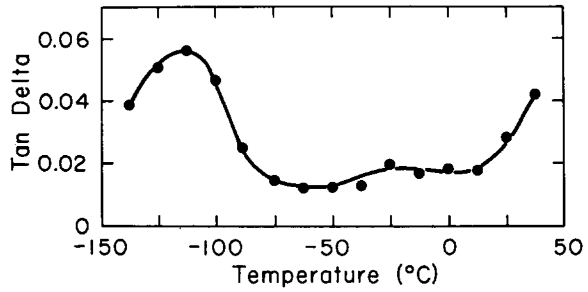

Figure 7 The tan δ of the unoriented HU4 polyethylene films measured by the DMA 982

time–temperature methodology developed in the theoretical section. To stay within the restrictions of the WLF equation, the crystalline and non-crystalline phase properties were separated by the two-phase compliance model of equation (6). Tashiro *et al.*[21] reported the in-plane shear compliance contribution of the crystalline phase to be 0.325×10^{-10} cm^2 dyn^{-1}. Three unoriented HU samples of varying degrees of crystallinity, listed in *Table 1*, were tested. *Figure 9* shows a plot of DMA complex compliance of the HU samples of *Table 2 versus* volume fraction crystallinity at a representative temperature of 20°C. At every temperature, a linear regression was performed on data points obtained from unoriented samples of various degrees of crystallinity similar to that demonstrated in *Figure 9*. The linear regression was forced to go through the average compliance of a 100% crystalline material as reported by Tashiro *et al.*[21]. This straight line is the graphic representation of equation (6) and thus its intercept at 0% crystallinity is the value of the average non-crystalline phase compliance. This two-phase modelling was performed on both the storage and loss compliances of the non-crystalline phase.

The time–temperature superposition was then performed on the extracted unoriented non-crystalline phase properties. In doing so, variable frequency thermograms of the DMA 982 were shifted employing the time–temperature relationship as described by the WLF equation with universal constants. Using the temperature at which each DMA data point was taken as reference, the entire variable frequency compliance thermogram was shifted to produce an isofrequency compliance thermogram. To compare these data with that of the Rheovibron, a constant frequency reduction of the variable frequency data of DMA at 11 Hz was reconstructed. This is the frequency at which all polyethylene samples were tested on the Rheovibron. *Figure 10* shows the calculated non-crystalline phase storage and loss compliance data of the DMA 982 and its constant frequency reduction. The values are within 2% of each other and the thermograms are practically the same and well within the bounds of experimental reproducibility. This is to be

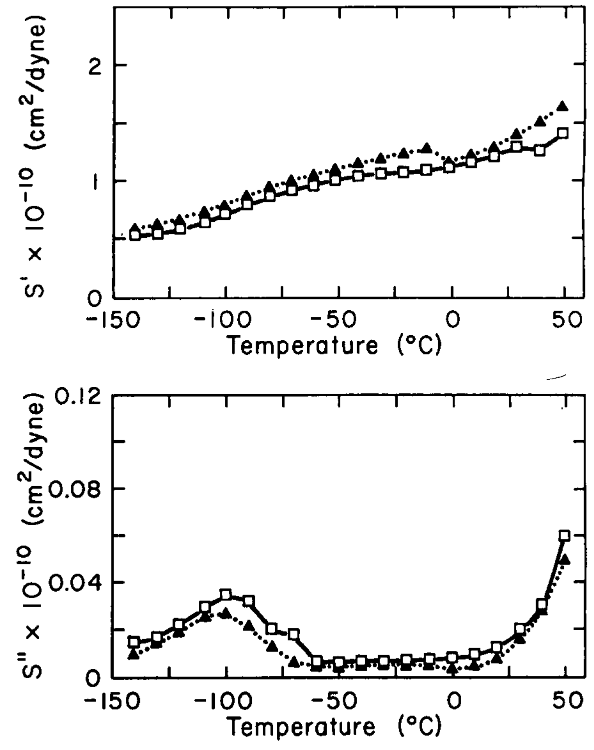

Figure 8 The storage and loss compliances of the oriented H1 polyethylene films in the draw direction (□——□) and transverse to it (▲····▲) measured by the DMA 982

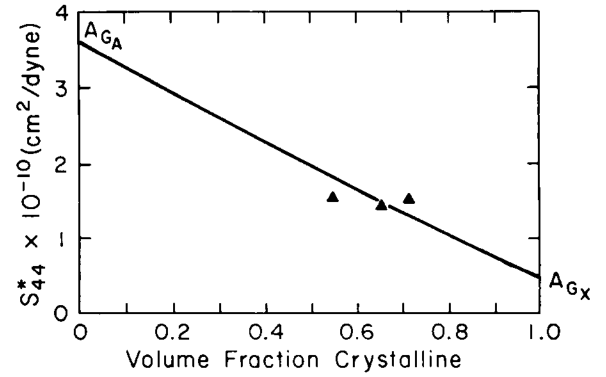

Figure 9 The complex compliance of unoriented HU polyethylene films of varying degrees of crystallinity. The least-squares fit was forced to go through the theoretical intrinsic compliance of the crystalline phase. ———, Theoretical; ▲, unoriented PE films

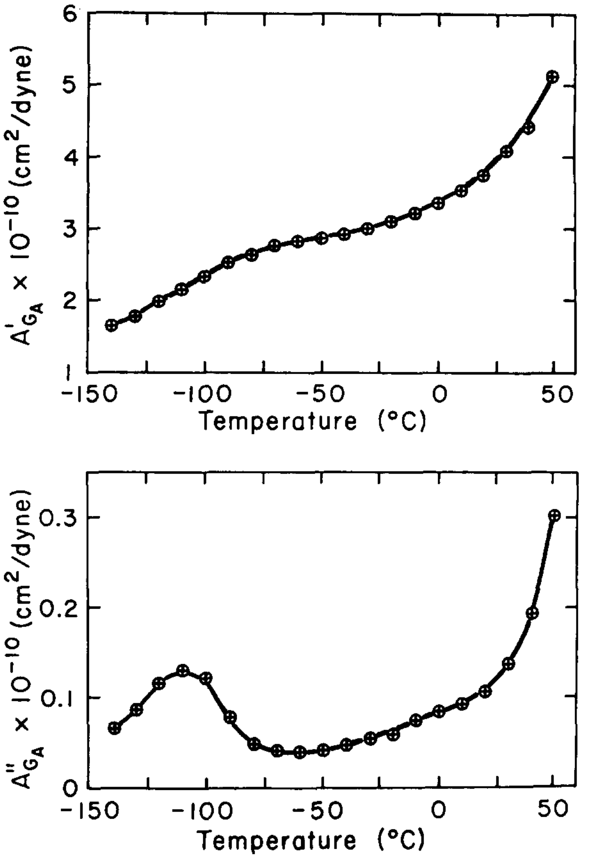

Figure 10 The variable frequency data (+) and the constant frequency reduction (○) of the non-crystalline phase storage and loss compliances of the unoriented HU4 polyethylene film

expected since the change in frequency throughout the experiment is only 6 Hz, a fraction of a decade. Thus, it can be concluded that, within the small changes of frequency, the DMA 982 data are close to the constant frequency data. If the changes in frequency are large, the time–temperature superposition along with the proper WLF constants can provide accurate constant frequency reduction of the data. The non-crystalline phase storage and loss compliances can be recombined with their crystalline phase counterparts according to the two-phase model of equation (12) to predict time–temperature shifted bulk compliances as well. When this was done for the unoriented HU4 polyethylene samples, the results were practically the same as those of *Figure 11* within the accuracy of the data. These results were also measured against true fixed frequency data obtained from the DMA 983 and are included in *Figures 15a* and *15b* and discussed in a later section.

Mode-of-deformation analysis

The mode of deformation of the DMA 982 was also investigated in relation to the tensile mode of deformation of the Rheovibron. The relationship between tensile compliance S_{33} and shear compliance S_{44} is given in a fashion similar to equation (15) as:

$$S_{44} = 2(1 + v)S_{33} \tag{21}$$

In examining these series of polyethylenes, Wedgewood and Seferis[9] extracted a Poisson's ratio of 0.45 supported by Waterman's dynamic results[22]. If the mode of deformation of the DMA is shear-dominated, then its compliance should relate to the compliance measured by the Rheovibron by $2(1 + v)$. This can be demonstrated either by the dynamic compliance values or, more accurately, by the non-crystalline phase compliance A_{Ga} extracted from the two-phase model of equation (6) in the manner demonstrated earlier. *Figure 12* shows the non-crystalline phase shear compliance A_{Ga} predicted from the Rheovibron's non-crystalline tensile compliance A_a using:

$$A_{Ga} = 2(1 + 0.45)A_a = 2.9A_a \tag{22}$$

This is plotted against the independent measurement of the non-crystalline phase compliance of the DMA 982. The agreement is good considering the extrapolation to zero crystallinity in calculating the non-crystalline phase

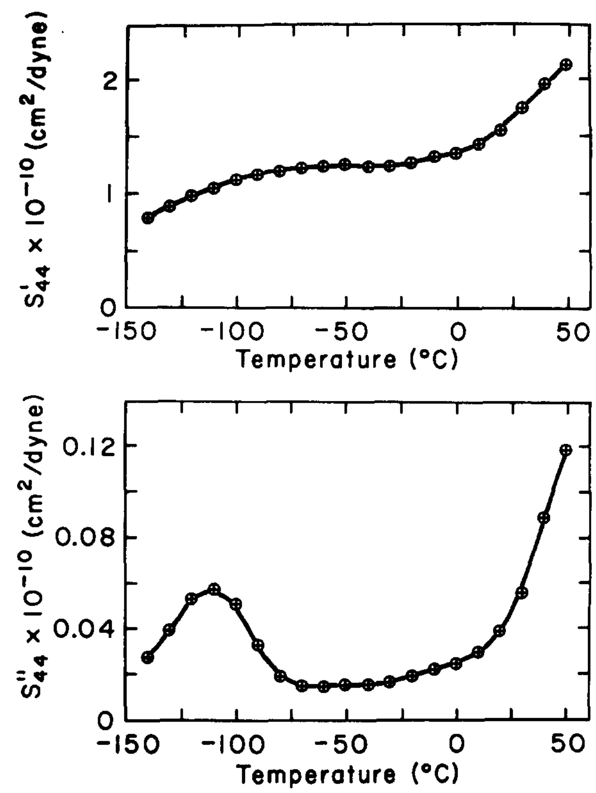

Figure 11 The variable frequency data (+) and constant frequency reduction (○) of the bulk storage and loss compliances of the unoriented HU4 polyethylene film

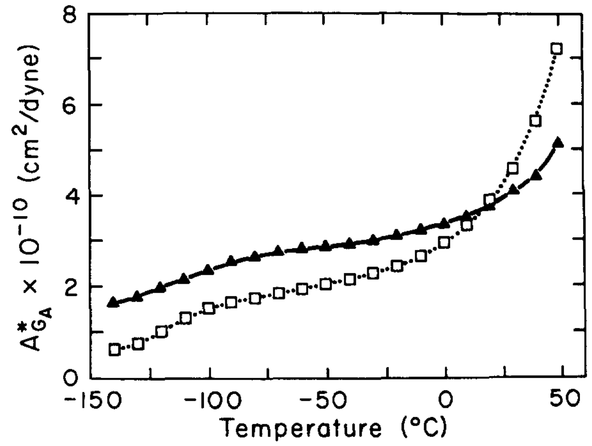

Figure 12 The complex compliance of the non-crystalline phase of the unoriented HU4 polyethylene films as measured by the Rheovibron (□····□) and the DMA 982 (▲——▲). The DMA thermogram is the result of the division of actual data by $2(1 + v)$

compliance A_{Ga}. Thus, it may be concluded that the mode of deformation in the DMA is shear-dominated when proper sample dimensions within the horizontal clamps are utilized.

Figure 8 shows the storage and loss compliances of the H1 polyethylene films at 0° and 90° as measured by the DMA 982. Macroscopic theory of elasticity showed that a uniaxially oriented solid has the same compliance along and transverse to the draw direction only if that compliance is measured under a shear mode of deformation. If the mode of deformation is not shear, the compliances would be different. This was demonstrated by equations (16) and (17). Within the accuracy of the experiments, the data are again essentially equivalent, evidence that the mode of deformation is indeed shear-dominated.

Figure 13 shows the storage and loss compliances of the H1 polyethylene film at 0° and 90° and the compliances of an unoriented HU4 polyethylene film of similar volume fraction crystallinity. Microscopic two-phase theory of elasticity, as detailed earlier, showed that, for a uniaxially oriented solid, the compliances along and transverse to the draw direction are equal to the compliance of an unoriented sample of the same solid and with the same volume fraction crystallinity, only if the mode of deformation is shear-dominated. This has also been theoretically shown to be true for the crystalline phase of polyethylene by McCullough *et al.*[23]. Within the accuracy of the experiments, the data are the same, evidence that the mode of deformation is shear-dominated. The shear-dominated deformation mode in the DMA 982 and 983 has been further validated by the analysis of Dillman and Seferis[24]. *Figure 14* shows the storage and loss compliances of the H1 polyethylene film measured by the Dynastat with the tensile clamps.

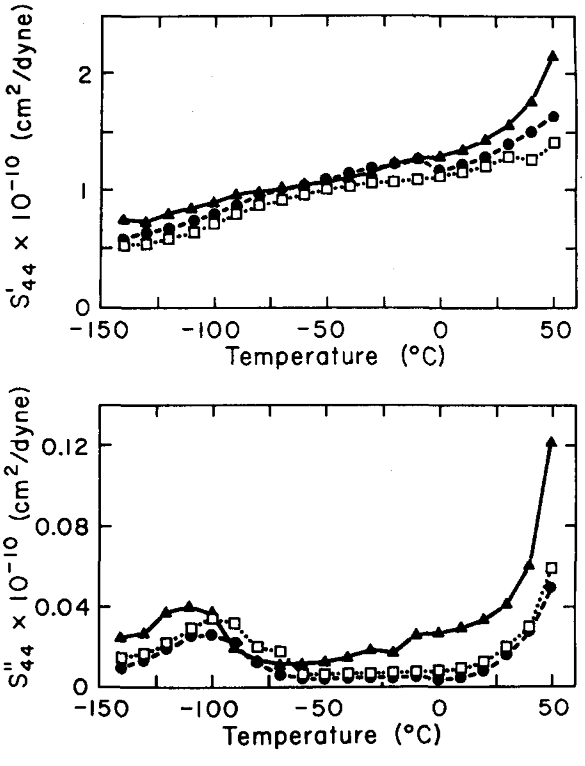

Figure 13 The storage and loss compliances of the oriented H1 polyethylene films in the draw (□····□) and transverse (●——●) directions as well as the storage and loss compliances of the unoriented HU4 films (▲———▲) measured by the DMA 982

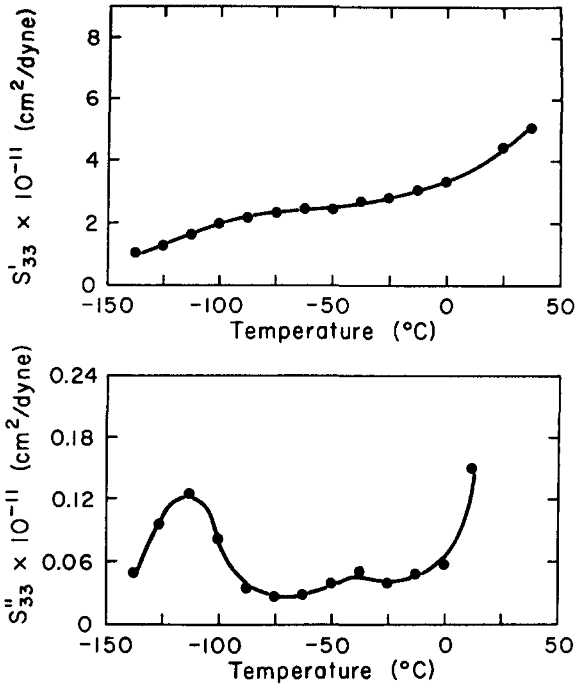

Figure 14 The storage and loss compliances of the oriented H1 polyethylene films in the draw direction measured by the Dynastat

Table 3 The sonic shear modulus of H1 and HU4 polyethylene films at 23°C

	Sonic compliance ($\times 10^{-10}$ cm^2 dyn^{-1})	
Film	Tensile	Shear
HU3	0.585	1.760
HU4	0.427	1.275
HU10	0.716	1.420
HU1 at 0°	0.3094	1.429
HU1 at 90°	0.4239	1.429

Comparison of *Figures 5* and *14* shows that the data obtained from both the Dynastat and the Rheovibron on uniaxially oriented H1 films are in good agreement. Sonic data of these polyethylene films taken at 5000 Hz and at room temperature are summarized in *Table 3*. Wedgewood and Seferis showed that these room-temperature sonic data are in agreement with the Rheovibron tensile data 10°C below room temperature[7,8]. In essence, this time–temperature superposition accounts for the difference in test frequencies of the Rheovibron and the sonic experiments. The agreement of tensile sonic data with the Rheovibron and the Dynastat, and the shear sonic data with the DMA is reasonably good.

Figures 15a and *15b* show master plots of all data for H1 polyethylene films tested in the draw direction where all data are translated to their shear or tensile equivalents on a common basis by a factor of $2(1+\nu)$ as detailed earlier. The data from various instruments are within 10% of the Rheovibron values. On a common deformation basis, data from all the instruments are in good agreement.

CONCLUSIONS

The dynamic mechanical responses of a number of

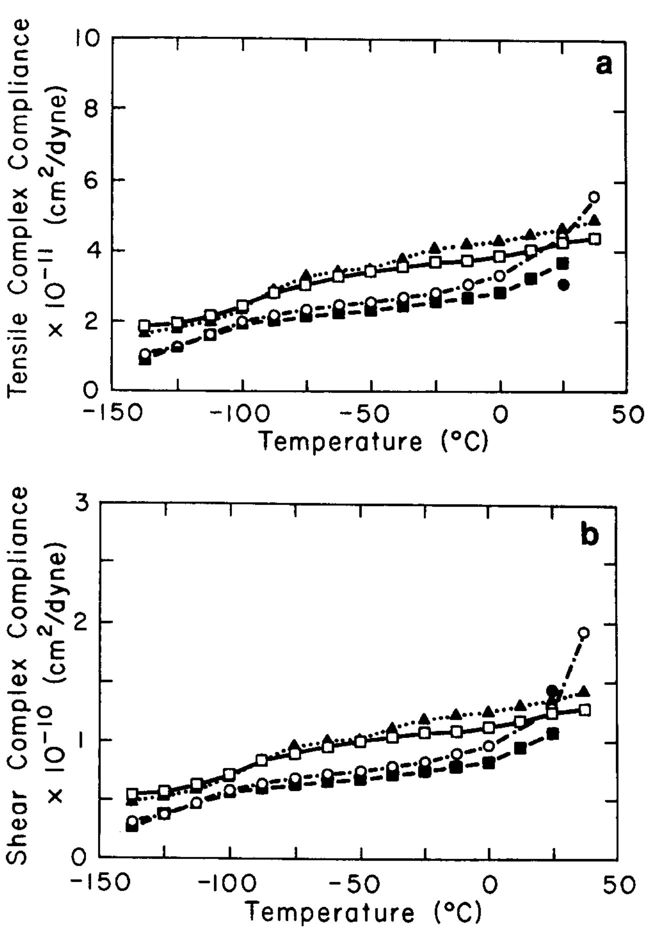

Figure 15 Master plots of (a) the complex tensile compliance and (b) the complex shear compliance of the H1 polyethylene films in the draw direction as measured by: ■—■, the Rheovibron; ○-·-○, the Dynastat; □———□, the DMA 982; ▲····▲, DMA 983; and ●, the sonic pulse propagation meter

instruments were uniquely correlated for time–temperature dependencies and mode of deformation. In this approach, the Williams–Landel–Ferry superposition, routinely applied to amorphous polymers, was applied to semicrystalline polyethylene. The mode of deformation was analysed by anisotropic macro- and micromechanical descriptions of the material's viscoelastic response. The experiments performed at various frequencies and temperatures were shown to be comparable to experiments at other frequencies and temperatures through the application of time–temperature superposition principles as well as other viscoelastic models. In this fashion, tensile and shear compliance data of a set of well characterized polyethylene samples were analysed. The DuPont DMA 982 and 983, Dynastat and sonic responses of these films were analysed against the Rheovibron values. Based on theoretical and experimental analysis of the DMA 982 and 983, it was shown that, for appropriate sample dimensions, these instruments operate under a shear-dominated mode of deformation. It was also shown that variations in frequency during the DMA 982 and 983 thermal scans do not significantly affect the dynamic mechanical results. The Dynastat equipped with a new clamp design provided results that were in excellent agreement with the Rheovibron data. Sonic shear and tensile compliances also showed good agreement with other shear and tensile results when corrected for their higher test frequency. Collectively, then, this study clearly showed that data from various instruments can be compared with one another as long as careful and proper data and instrument analyses are performed.

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