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Characterization of Viscoelastic Properties of Polymeric Materials Through Nanoindentation

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Abstract

Nanoindentation testing was used to determine the dynamic viscoelastic properties of eight polymer materials, which include three high-performance polymers and five densities of high-density polyethylene. It was determined that varying the harmonic frequency of nanoindentation does not have a significant effect on the measured storage and loss moduli of the polymers. Agreement was found between these nanoindentation results and data from bulk Dynamic Mechanical testing of the same materials. Varying the harmonic amplitude of the nanoindentation had a limited effect on the measured viscoelastic properties of the resins. However, storage and loss moduli from nanoindentation were shown to be sensitive to changes in the density of the polyethylene.

Introduction

Within the last five years, the materials development community has witnessed a tremendous increase in the interest in nanostructured materials. In general, a nanostructured material is defined to be a material with at least one constituent at a characteristic length scale on the order of tens of nanometers or less. Many of these new nanostructured materials have been designed for use in engineering applications where bulk properties such as stiffness and strength are the primary properties for evaluating performance. The use of these nanostructured materials in macroscale engineering applications, therefore, involves the development of accurate constitutive models, material property data, and quantification of material attributes as they relate to processing variables. Ultimately, this requires a multi-scale approach that may range more than 12 orders of magnitude, and relies on accurate structure-property relationships derived from careful material characterization and validated material models.

A computational materials approach to coupling the modeling and characterization methods across the scale levels has been proposed [1]. Within the context of this approach, it is

recognized that quantitative material property characterization at the microscale and below is a key ingredient for success. Typical bulk property measurements are unable to provide the spatial or force resolution necessary to develop constituent properties for nanostructured materials. However, with the goal of accurate material testing in mind, recent developments in nanoindentation have shown that it may be a promising method of measuring the mechanical properties of materials at sub-micrometer length and sub-mN load scales, thus allowing individual constituents and local regions of heterogeneous materials to be characterized individually. The ability to measure properties on the nanometer length scale is particularly important for the development of nanostructured, polymer composite materials in which the localized material structure can have a significant impact on the overall or bulk behavior.

Before approaching the problem of measuring localized properties of nanostructured composites, confidence must be developed in the measurement methods as applied to homogeneous polymer materials. In particular, the time-dependent nature of most polymers must be accounted for when performing localized measurements of properties. The basic methods for measuring static elastic stiffness and strength properties [2] and quasi-static viscoelastic properties [3-10] of polymers through nanoindentation have been developed. However, the dynamic viscoelastic characterization of polymer materials through nanoindentation has not been studied in detail [11-15]. It can be assumed that most polymers exhibit time-dependent or viscoelastic behavior, the degree of which is dependent on intrinsic material properties, such as density, and external variables, such as temperature. For characterizing time-dependent behavior, dynamic viscoelastic testing offers an advantage over quasi-static methods by significantly decreasing testing time through the measurement of properties over a range of frequencies rather than extended time. Given the lack of published data on viscoelastic characterization of polymers using nanoindentation, it is clear that consistent and accurate methods for obtaining the dynamic viscoelastic properties of polymers and their composites through nanoindentation need to be established in order to facilitate the use and development of these materials.

Therefore, the objectives of the current paper are to establish experimental methods for dynamic nanoindentation, to investigate the ability of these nanoindentation methods to determine the dynamic viscoelastic response of polymer materials, and to compare the results from these tests to bulk properties measured using standard Dynamical Mechanical Analysis (DMA) tests for the same polymer resins tested under similar conditions. To accomplish these objectives, a series of nanoindentation and DMA tests were performed on eight polymer systems, including three high-performance resins intended for elevated-temperature conditions, and five resins of high-density polyethylene (HDPE). These materials were chosen to produce a test plan that allowed for sensitivity studies of the results to systematic variations in intrinsic material properties. To study the relative influence of test parameters, the dynamic nanoindentation tests were conducted at room temperature using a range of harmonic amplitudes and harmonic frequencies. Results from these tests, in the form of storage and loss modulus, are quantified and compared.

Materials and Specimens

In this study, eight polymer materials were used for both nanoindentation and DMA viscoelastic characterization. The first material, designated 5260, is a modified bismaleimide thermoset polymer manufactured by BASF Corporation. The second material, designated 8320, is a

thermoplastic polyarylsulfone polymer manufactured by Amoco Corporation. The third material, designated LaRC-SI, is a thermoplastic polyimide manufactured by Imitech Incorporated with a 1% stoichiometric offset [16]. These three polymers were chosen for the current study because they represent typical polymers used for aerospace applications with glass transition temperatures of at least 220º C. The remaining five materials were high-density polyethylene (HDPE) at five different densities: 0.9489, 0.9495, 0.9503, 0.9671, and 0.9691 g/cc; and were manufactured by Aldrich Corporation in pellet form. The densities of these materials were measured in their final form using a density gradient column. All seven of the materials were tested in solid form with the LaRC-SI and HDPE test specimens cut from plaques that were fabricated via compression molding at NASA Langley Research Center.

For the nanoindentation specimens, small coupons were cut from the test materials with approximate dimensions 10 mm × 10 mm with a thickness of at least 3 mm. The specimens were mounted onto the nanoindentation fixture using a cyanoacrylate-based adhesive. A Buehler polishing wheel and 3 μm alumina polishing solution were used to prepare the testing surface of each nanoindentation specimen. Three DMA specimens, per material type, were also cut with approximate dimensions of 50 mm × 12 mm and a thickness equal to the nanoindenter test specimen thickness.

Dynamic Nanoindentation Testing

The nanoindentation tests were performed at room temperature using a MTS Nano Indenter® DCM (Dynamic Contact Module) system[1] with a Berkovich indenter tip. The shape of the Berkovich tip is a three-sided pyramid measuring approximately 2000 nm along its base. For the DCM system, the displacement resolution is 0.0002 nm, and the loading capacity and resolution are 10 mN and 1 nN, respectively. A schematic of the nanoindentation system and indentation process is shown in Fig. 1. Referring to Fig. 1, during testing a force is applied onto the indenter column, which drives the indenter head into the material while the displacement of the indenter column is continuously monitored. The Continuous Stiffness Measurement (CSM) method was used, which allowed for a continuous measure of the dynamic stiffness of the material throughout the loading process by using a low magnitude oscillating force superimposed onto the overall quasi-static force signal. The displacement response is measured at the same frequency as the applied oscillating force, and any resulting phase lag can be related to the loss factor or damping of the material.

The apparatus shown in Fig. 1 can be modeled as shown in Fig. 2. The values of the support spring stiffness, K_s, the load frame stiffness, K_f, the indenter damping, D_i, and the indenter mass, m, are known *a priori* (provided by the manufacturer). The stiffness and damping of contact, S and D_s, respectively, depend on the materials and conditions at the contacting surfaces. The overall response of the system can be used to determine these parameters, which are subsequently used to determine the linear-viscoelastic properties of the tested material.

[1] The use of trademarks or names of manufacturers in this report are for accurate reporting and do not constitute an official endorsement, either expressed or implied, of such products or manufacturers by the National Aeronautics and Space Administration.

In a manner similar to that usually used with viscoelastic materials [17], if it is assumed that the load frame stiffness, K_f, provides the major contribution to the total stiffness such that K_f approaches ∞ , then the force balance on the model shown in Fig. 2, in the contact direction, z, is given by

$$F(t) = m\ddot{z}(t) + (D_i + D_s)\dot{z}(t) + (K_s + S)z(t) \tag{1}$$

The driving or oscillating force is

$$F(t) = F_0 e^{i\omega t} \tag{2}$$

where F_0 is the force amplitude and ω is the harmonic frequency. The assumed particular solution for the displacement is

$$z(t) = z_0 e^{i(\omega t - \phi)} \tag{3}$$

where z_0 is the displacement amplitude and ϕ is the phase angle, associated with damping, between the applied force and resultant displacement. Substitution of Eqs. (2) and (3) into (1) and simplifying yields

$$\frac{F(t)}{z(t)} = A_1 + iA_2 \tag{4}$$

and

$$\frac{F_0}{z_0} = (A_1 \cos\phi + A_2 \sin\phi) + i(A_2 \cos\phi - A_1 \sin\phi) \tag{5}$$

where the constants A_1 and A_2 are

$$\begin{aligned} A_1 &= K_s + S - m\omega^2 \\ A_2 &= (D_i + D_s)\omega \end{aligned} \tag{6}$$

The phase angle can also be written in terms of the ratio between the imaginary and real components such that

$$\tan\phi = \frac{\mathrm{Im}\left(F(t)/z(t)\right)}{\mathrm{Re}\left(F(t)/z(t)\right)} \tag{7}$$

The magnitude of the ratio of the force and displacement amplitudes is

$$\left|\frac{F_0}{z_0}\right| = \sqrt{\left[\mathrm{Re}\left(F_0/z_0\right)\right]^2 + \left[\mathrm{Im}\left(F_0/z_0\right)\right]^2} \tag{8}$$

Substitution of Eqs. (4), (5), and (6) into Eqs. (7) and (8), and solving simultaneously for the material stiffness and damping yields

$$S = \left|\frac{F_0}{z_0}\right|\cos\phi + m\omega^2 - K_s \tag{9}$$

and

$$\omega D_s = \left|\frac{F_0}{z_0}\right|\sin\phi - \omega D_i \tag{10}$$

The force and displacement amplitudes and the harmonic frequency of the applied force oscillations are measured by the nanoindentation system. The quantities in Eqs. (9) and (10) are subsequently used to determine the elastic and viscous components of the material behavior.

At a given frequency, the dynamic or oscillatory force, such as given in equation (2), will cause an oscillatory strain response at the same frequency but lagging behind by the phase angle, ϕ [17]. The ratio between the complex strain amplitude and the stress amplitude is defined as the complex compliance, J. The complex compliance and complex stiffness are reciprocal and the magnitude of the complex compliance is simply the inverse of the magnitude of the complex modulus, E, (i.e. $|J| = 1/|E|$) [17]. For linear-viscoelastic materials, it is often convenient to express the overall constitutive behavior in terms of the complex modulus given by

$$E = E' + iE'' \tag{11}$$

where the storage modulus, E', is in phase with the strain and characteristic of elastic behavior, and the loss modulus, E'', is characteristic of internal damping. By implementing the elastic solution for the Young's modulus from nanoindentation [18-20] and the elastic-viscoelastic correspondence principle [17], the storage modulus of a polymer determined through nanoindentation is given by

$$E' = \frac{S}{2\beta}\sqrt{\frac{\pi}{A}} \tag{12}$$

where β is a constant that depends on the geometry of the indenter ($\beta = 1.034$ for the Berkovich indenter that is used in the present study) and A is the projected contact area of the indenter. The projected contact area is determined as a function of contact depth (Fig. 1) using an empirical function which is established by indenting a material with a known modulus, as outlined by Oliver and Pharr [2]. Similarly, the loss modulus is

$$E'' = \frac{\omega D_s}{2\beta}\sqrt{\frac{\pi}{A}} \tag{13}$$

where ωD_s is given by Eq. (10).

Dynamic Mechanical Analysis Testing

Dynamic Mechanical Analysis (DMA) testing is a standard thermal-mechanical analysis technique for characterizing viscoelastic properties of polymers [21, 22]. The objectives of the DMA tests were to measure macro-scale or bulk storage modulus, using conditions similar to the nanoindentor, and then perform a direct comparison of results from the two types of tests as a function of material type and test parameters. As with the dynamic nanoindentation tests, the DMA tests were performed at room temperature on all the materials. The DMA test apparatus was commercial equipment, and the test procedures were based on recommendations supplied by the equipment manufacturer.

Briefly, in the DMA testing used for this study, an oscillatory force (in three-point bending mode) was applied at a selected frequency onto a polymer sample, and the resultant dynamic storage and loss modulus were calculated using the vendor-supplied data reduction routines. The test equipment allowed testing at multiple frequencies, and the analysis of the data was similar to that outlined in the previous section.

Contact Area Calibration

In the course of development and verification of new test methods, careful attention must be paid to calibration procedures. One of the suggested methods for calibration of the nanoindenter is to perform a series of indents on a standard material. The standard material should have uniform, well-known material properties that can be reliably used by the calibration routines to establish a projected contact area for the indenter tip. For materials with high, through-the-thickness stiffness, such as metallic thin-films, the projected contact area, A (Eqs. (12) and (13)), is typically determined by using a fused silica calibration standard. However, because of the relatively low moduli of the test polymers with respect to the fused silica, the projected contact area was instead determined using the 5260 material as a calibration standard. This material was chosen for the calibration because of its well-understood mechanical behavior in a variety of environmental conditions. The specific steps in the calibration procedure were similar to that discussed elsewhere [2, 6], however, a brief discussion is provided herein.

Prior to performing calibration and determining the contact area, the storage modulus of the 5260 material at room temperature was measured using a DMA test over a wide range of frequencies, and found to have a mean value of 4.5 GPa. With this storage modulus calibration data now available, twenty-five indentations were made onto the 5260 nanoindentation calibration specimen, and the average contact area was then subsequently determined as a function of contact depth by using Eq. (12), a fifth-order polynomial curve fit relating the tip area to contact depth, and the known storage modulus measured via DMA. Because of the different stress states that are present in the nanoindentation and DMA tests, it is assumed in this calibration procedure that the properties of the 5260 are the same in tension and compression.

Testing Procedures

The baseline procedure for the nanoindentation tests was to apply the load to the specimen at a strain rate of 0.05 s^{-1}, harmonic frequency of 75 Hz, and harmonic amplitude of 1 nm, which represent default settings of the system. The storage and loss moduli were calculated for an indentation depth range of 500 to 1400 nm. Up to fifteen indentations were averaged to provide a single data point. The baseline procedure for the DMA tests was to cycle the specimen at a harmonic frequency of 1 Hz and harmonic amplitude of 15 μm, which represent typical settings used for the system. Three separate DMA specimens were tested for each material. All nanoindentation and DMA tests were conducted at room temperature.

To aid in the complete understanding of the relative influence of test parameters during indentation testing, harmonic amplitude and harmonic frequency were selected for study and systematically varied. To study the effect of harmonic amplitude on the storage and loss moduli, a set of indentation tests were performed on each material in which the harmonic amplitude was varied from the baseline (1 nm) to 50 nm, while all other parameters remained unchanged. Similarly, the harmonic frequency was varied from 5 Hz to 115 Hz with the other parameters kept constant to examine its effect on the measured viscoelastic properties. To facilitate a direct comparison in measured response, the same materials were also tested with the DMA, at frequencies in the same range (5 to 115 Hz) and with harmonic amplitudes varied from 5 to 50 μm.

In a manner similar to the test parameter study, the relative influence and sensitivity of the indentation testing to material composition was determined by testing materials with distinct differences in engineering properties, and in the case of the HDPE, subtle yet systematic variations in material density.

Results and Discussion

Results from the nanoindentation and DMA tests are presented (Figs. 3-7 and Tables 1 and 2) in terms of storage and loss modulus as a function of test variables or material type. On all plots and tables, the error bars and uncertainties at specific data points represent the standard deviation of the mean as measured through repetitive tests.

Typical storage and loss moduli for the 5260, 8320, LaRC-SI, and HDPE (density = 0.9671 g/cc) are provided in Fig. 3 over the entire depth range tested at a harmonic amplitude and frequency of 10 nm and 75 Hz, respectively. The differences in elastic stiffness between material types are evident by the relative location of the storage modulus curves. For the 5260, 8320, and LaRC-SI polymers, surface penetration of 200 to 400 nm was required before the storage modulus obtained a relatively constant value. This is most likely because of increased experimental uncertainties that exist for shallow indentation depths [7]. For the HDPE, a larger surface penetration of 600 nm was required. A likely cause of this difference in behavior is due to the effects of specimen polishing which is explained by the fact that the HDPE, which has a glass transition temperature below room temperature, was more likely to be affected by the local heating from polishing friction than the high glass transition temperature materials (i.e. 5260,

8320, LaRC-SI). For the loss moduli, similar trends exist in which the high glass transition temperature polymers and the HDPE obtain constant loss moduli at surface penetrations around 100 nm and 600 nm, respectively. Based on these observed trends in storage and loss modulus, an average modulus value was determined for each test by using the mean value of the modulus between 500 and 1400 nm of indentation depth.

To put these results from the nanoindentation tests in perspective, the average measured storage and loss moduli for a range of harmonic amplitudes are plotted in Fig. 4 for the 5260, 8320, LaRC-SI, and HDPE (density = 0.9671 g/cc). For the 5260 and 8320 materials, there was no significant influence of the harmonic amplitude on the viscoelastic properties. For the LaRC-SI and HDPE, the storage moduli decreased as the amplitude increased while the loss modulus did not change significantly. The decrease in storage modulus of the HDPE polymer was larger than that of the LaRC-SI. This indicates that the measured storage moduli of polymers with a low glass-transition temperature may be more dependent on the harmonic amplitude than those of high-performance polymers.

For the DMA tests, the measured storage and loss moduli for the same polymers examined in Fig. 4 are plotted in Fig. 5. For all four polymers, there was an increase in the DMA storage moduli over the range of harmonic amplitudes, with no significant influence of the DMA harmonic amplitude on the loss moduli. Comparing the data in Figs. 4 and 5, it is apparent that the trends in the storage moduli from the two methods disagree. The reason for this discrepancy in trends could be due to the different states of stress in the indentation specimen versus the DMA specimen (contact versus bending), which are a direct function of the differences in the test geometries and applied force amplitude magnitudes. In addition, the discrepancy could be partly due to the differences in the storage moduli of the surface and bulk materials.

The measured storage moduli of the 5260, 8320, LaRC-SI, and HDPE (density = 0.9671 g/cc) polymers for a range of harmonic frequencies are plotted in Fig. 6. The harmonic frequency did not have a significant effect on the storage moduli of any of the materials. For comparison purposes, the viscoelastic properties of these materials, determined using the DMA, was also plotted in Fig. 6. In general, there was good agreement between the nanoindenter and DMA test methods except for the case of the 8320 storage modulus data. In that case, the results reveal up to a 30% difference in storage modulus when comparing test methods. The source of this discrepancy is unknown, although it could possibly be due to changes is the properties of the polymer at the specimen surface during surface polishing or specimen storage.

The measured loss moduli of the 5260, 8320, LaRC-SI, and HDPE (density = 0.9671 g/cc) polymers for a range of harmonic frequencies are plotted in Fig. 7. Only a limited range of harmonic frequencies are shown in Fig. 7 to emphasize the trends at the higher frequencies. For all four materials the loss moduli increased measurably between the frequencies of 55 and 115 Hz. Also plotted in Fig. 7 are the loss moduli of these materials determined using the DMA test method. Based on these results, there was no significant effect of the harmonic frequency on the loss moduli. It should be noted that the magnitude of the loss moduli was quite small relative to those of the storage moduli, and therefore limits on measurement resolution can contribute to loss in accuracy of the data for both nanoindentation and DMA systems.

From the nanoindentation tests, the storage and loss moduli for all five material densities of HDPE are listed in Tables 1 and 2, respectively, for various harmonic amplitudes. In general, the results indicate that both storage and loss moduli increased with increasing material density. The storage moduli increased with decreasing harmonic amplitude, while there was no consistent trend with the loss moduli and harmonic amplitude, which was consistent with the nanoindentation results presented in Fig. 4, but not with the DMA data shown in Fig. 5.

Summary

In this study, the primary objectives were to explore the ability of nanoindentation testing to determine the dynamic viscoelastic properties of polymer materials and to quantify the relative influence of test parameters and material variations on the measured response. For comparison purposes, the viscoelastic data acquired from nanoindentation was directly compared to bulk viscoelastic data obtained from standard DMA tests on identical materials. The test variables investigated were harmonic frequency and harmonic amplitude. Eight distinct polymers were selected as the test materials. These eight materials consisted of three high-performance materials (8320, 5260, and LaRC-SI) and five density variations of polyethylene (HDPE).

Analysis of the test data revealed that over a wide range, variations in the harmonic frequency of the nanoindentation test did not have any significant effect on the measured dynamic storage and loss moduli of the polymers. For all cases, good agreement was found between results from the nanoindentation and results from DMA testing of the same materials, indicating that harmonic frequency is not a critical test variable for dynamic nanoindentation of these polymers. Conversely, it was found that varying the harmonic amplitude of the nanoindentation test may have a significant effect on the storage and loss moduli; however, that effect may be dependent on material selection. Comparison between nanoindentation and DMA results also reinforced the conclusion that selection of harmonic amplitude can be a critical factor when performing dynamic indentation tests.

In general, dynamic indentation testing was found to be sensitive to intrinsic differences in materials, even to the extent that small variations in material density resulted in measurable differences in storage modulus. For most of the cases investigated in this study, the comparison between the localized nanoindentation data and the bulk DMA data indicates that with proper attention to test parameters, dynamic nanoindentation can be useful for measuring viscoelastic properties of polymer materials and should find great utility when used as a characterization tool for inhomogeneous materials such as nanostructured polymer-based composites.

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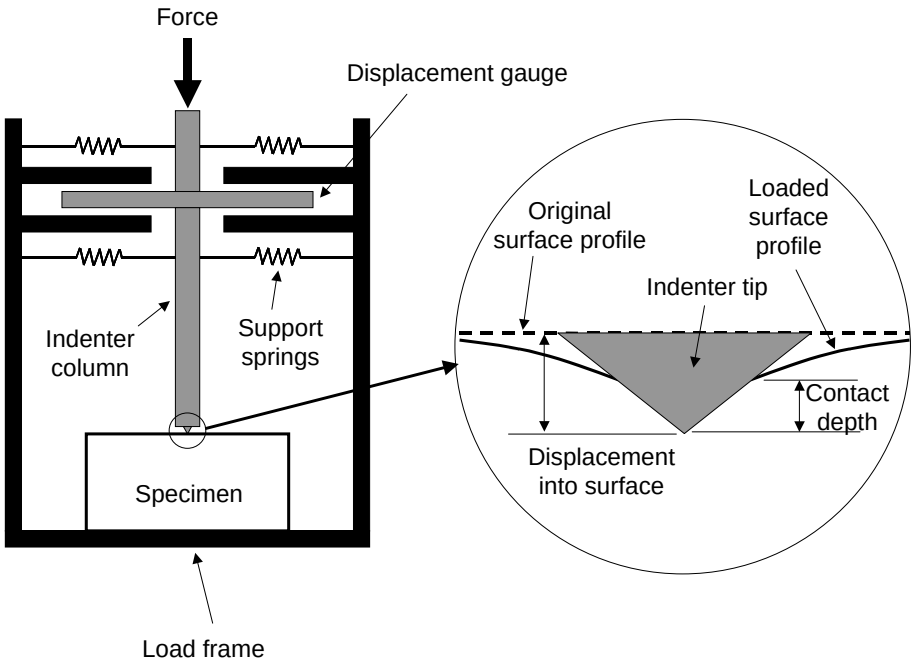

Fig. 1. Diagram of nanoindentation system

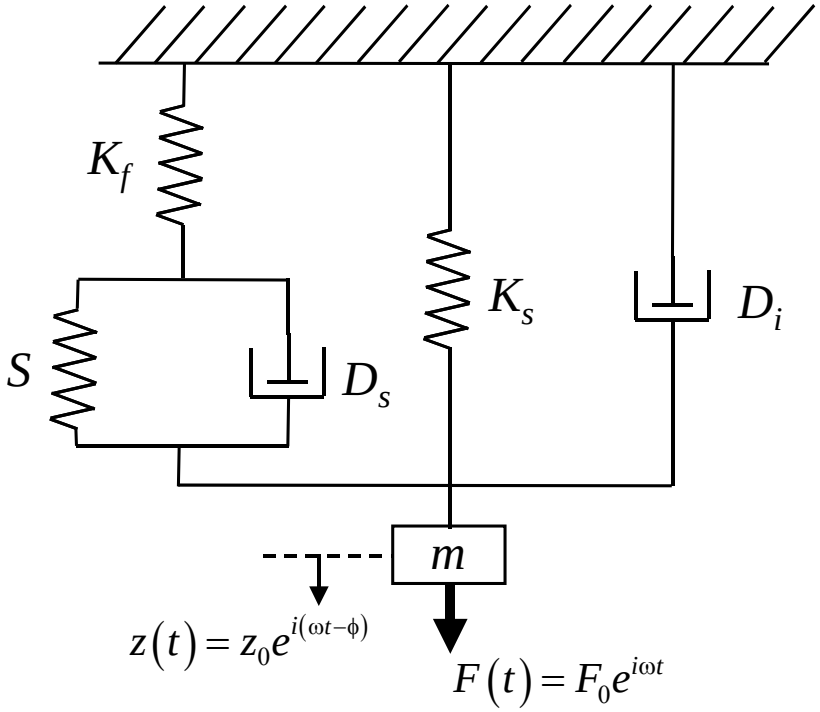

Fig.2. Mechanical model for nanoindentation

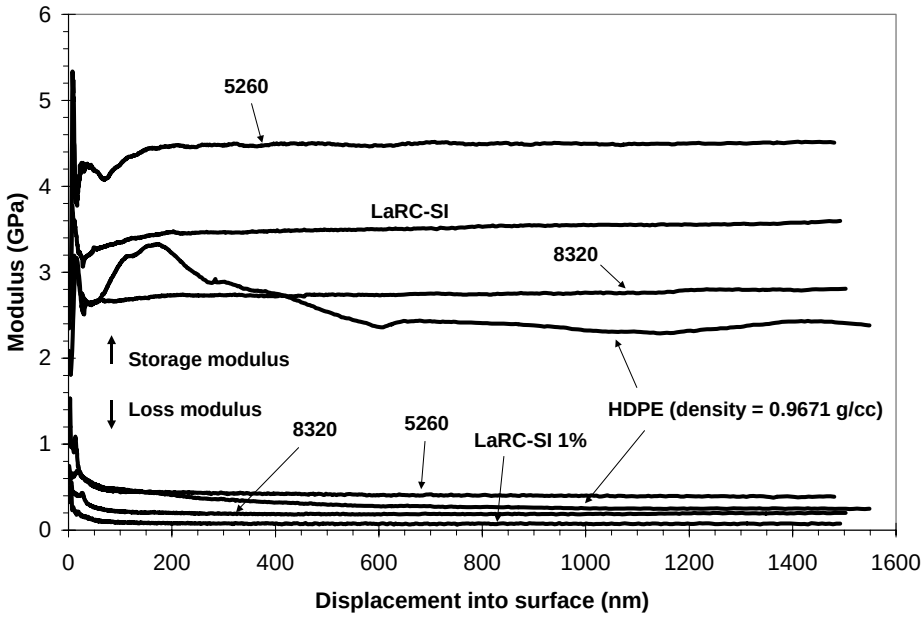

Fig. 3. Storage and loss moduli versus displacement into surface for nanoindentation tests for a harmonic frequency and amplitude of 75 Hz and 10 nm, respectively.

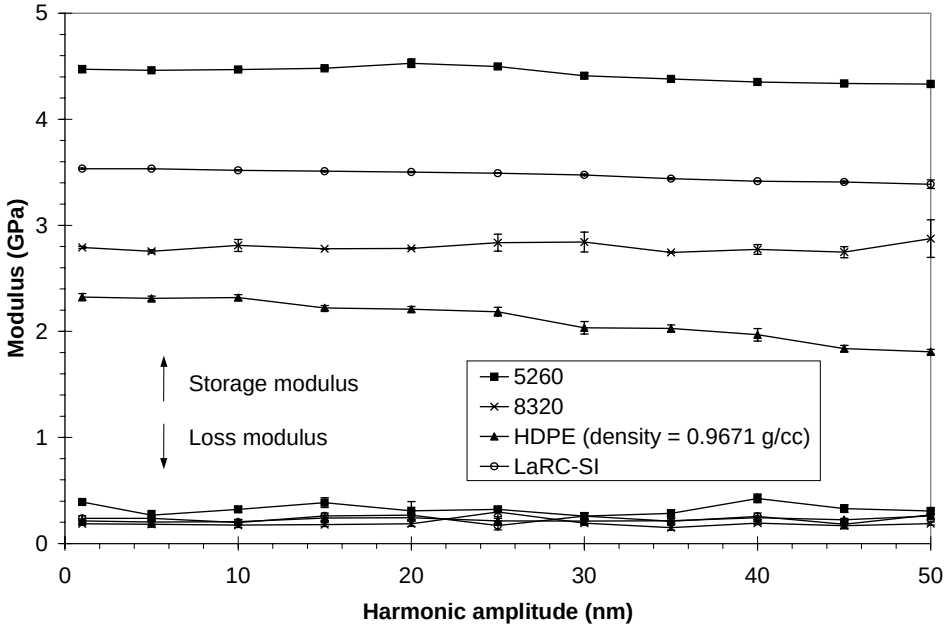

Fig. 4. Storage and loss moduli versus harmonic amplitude for nanoindentation tests for a harmonic frequency of 75 Hz, based on average values over the depth range of 500 to 1400 nm.

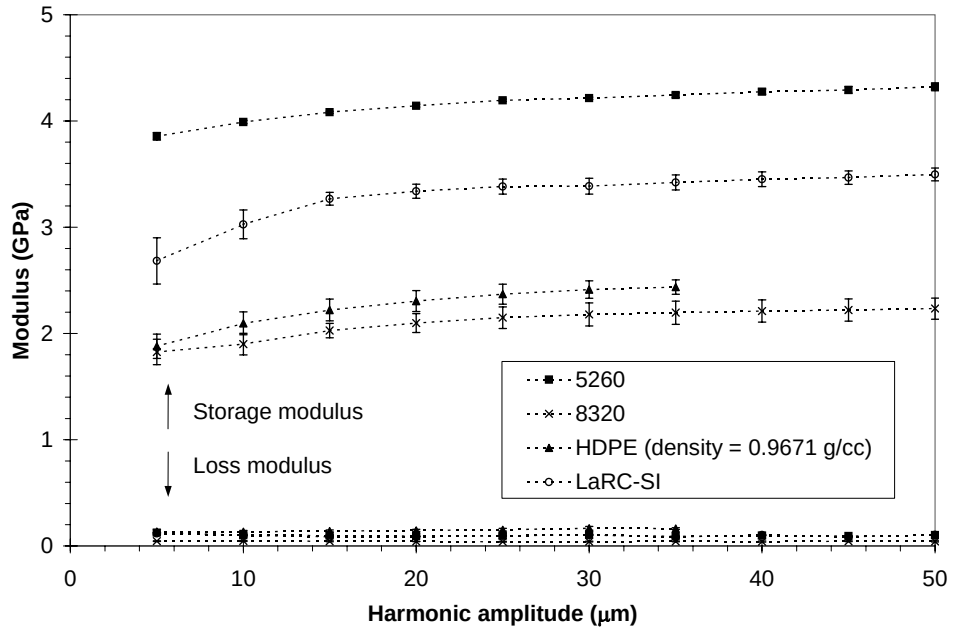

Fig. 5. Storage and loss moduli versus harmonic amplitude for DMA tests for a harmonic frequency of 1 Hz.

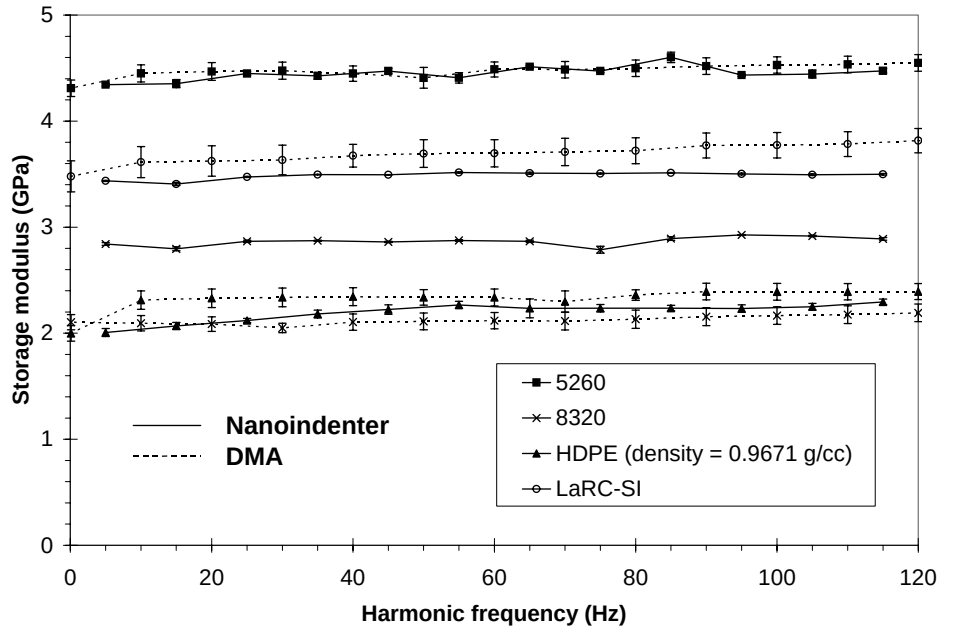

Fig. 6. Storage modulus versus harmonic frequency for both the nanoindenter and DMA test methods. For the nanoindentation data, the harmonic amplitude was 1 nm.

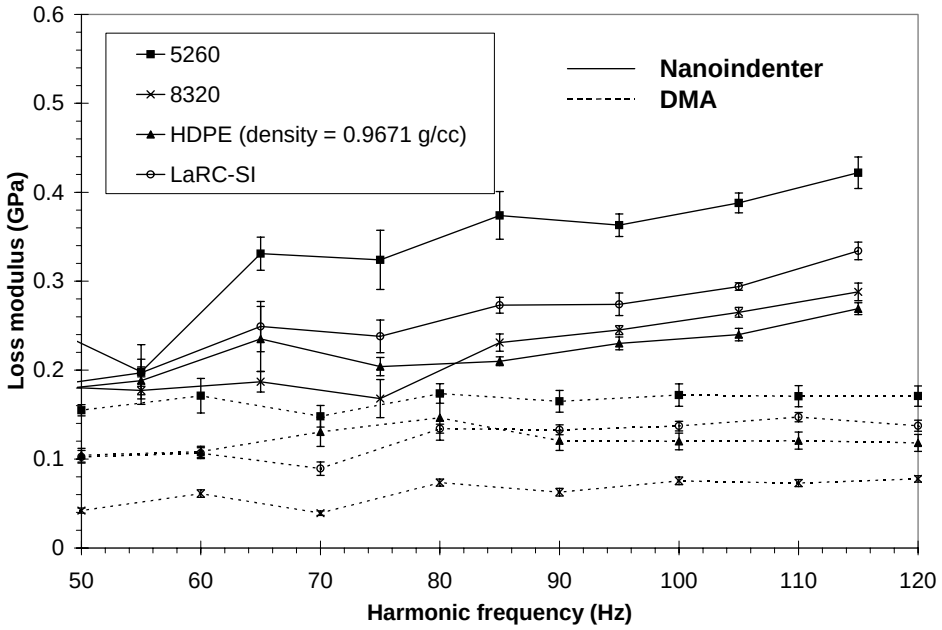

Fig. 7. Loss modulus versus harmonic frequency for both the nanoindenter and DMA test methods. For the nanoindentation data, the harmonic amplitude was 1 nm.

Table 1. Storage moduli of HDPE (in GPa) for various HDPE densities for the nanoindenter tests at a harmonic frequency and harmonic amplitude of 75 Hz and 1 nm, respectively.

Density (g/cc)	Harmonic amplitude = 1 nm	Harmonic amplitude = 15 nm	Harmonic amplitude = 30 nm	Harmonic amplitude = 45 nm
0.9489	1.17±0.02	1.15±0.01	1.06±0.01	1.11±0.02
0.9495	1.72±0.02	1.30±0.03	1.16±0.01	1.13±0.02
0.9503	2.04±0.03	1.92±0.04	1.66±0.01	1.52±0.02
0.9671	2.32±0.03	2.22±0.02	2.03±0.06	1.84±0.03
0.9691	2.48±0.03	2.28±0.03	2.13±0.05	1.89±0.02

Table 2. Loss moduli of HDPE (in MPa) for various HDPE densities for the nanoindenter tests at a harmonic frequency and harmonic amplitude of 75 Hz and 1 nm, respectively.

Density (g/cc)	Harmonic amplitude = 1 nm	Harmonic amplitude = 15 nm	Harmonic amplitude = 30 nm	Harmonic amplitude = 45 nm
0.9489	108±9	107±8	118±9	120±17
0.9495	172±8	147±14	135±5	167±9
0.9503	216±10	210±13	221±14	236±19
0.9671	213±18	241±26	212±25	224±13
0.9691	236±11	236±15	248±29	284±18