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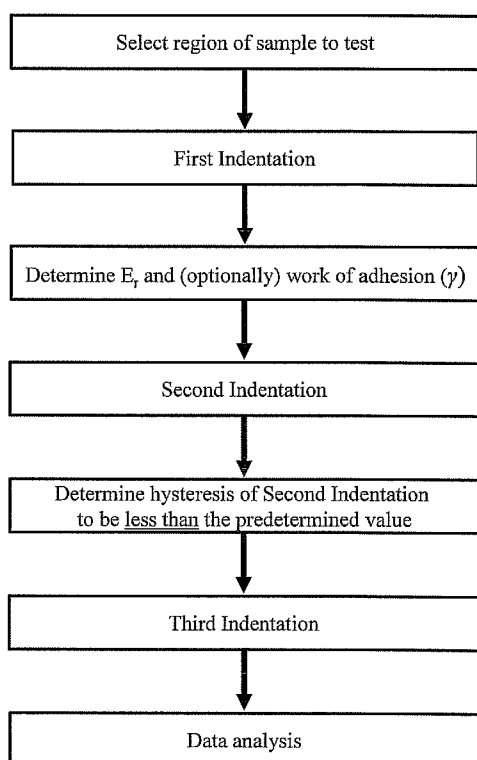
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(54) Title: PROCESS FOR DETERMINING VISCOUS, ELASTIC, PLASTIC, AND ADHESIVE (VEPA) PROPERTIES OF MATERIALS USING AFM-BASED OR CONVENTIONAL NANO-INDENTATION



(57) Abstract: A process is described for determining elastic modulus, plastic yield strain, and viscosity of a material, and the work of adhesion between the material and an indenter tip, using Atomic Force Microscopy-based or conventional nanoindentation. Specifically, the process includes a measurement method whereby a sequence of load-unload quasistatic indentations are performed in the vicinity of each chosen point on a sample. The loading- unloading curves are analyzed using a specific modeling algorithm to calculate multiple mechanical properties of the sample.

**FIGURE 14**



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**PROCESS FOR DETERMINING VISCOUS, ELASTIC, PLASTIC, AND  
ADHESIVE (VEPA) PROPERTIES OF MATERIALS USING AFM-BASED OR  
CONVENTIONAL NANO-INDENTATION**

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**STATEMENT OF GOVERNMENT INTEREST**

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**FIELD OF THE INVENTION**

The invention relates to methods for the determination of materials properties utilizing Atomic Force Microscopy (AFM) and/or nanoindenters; in particular the invention relates to devices, systems, and methods for the simultaneous determination of viscous, elastic, plastic, and adhesive properties of materials comprising a testing protocol and associated data analysis model.

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**BACKGROUND OF THE INVENTION**

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Materials on the nanoscale, those with structures measured in nanometers (<100 nm), offer revolutionary capabilities and performance based on the unique advantages of ultra-small structure. The promise of such nanomaterials cannot be fully realized, however, until the relationships between structure and physical properties are understood at the nanometer level.

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Atomic Force Microscopes (AFM) and nanoindenters have been used to determine mechanical properties of a material by applying a load force to the probe tip to cause an indentation to be formed in the material surface, and then releasing (unloading) the force from the tip. Thus, by loading and unloading the probe tip, a plot of load versus indenter displacement can be obtained which permits determination of both plastic

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(permanent) and elastic (resilient) deformation properties for the material being tested.

Nanoindentation differs from AFM methodology in the aspect that the probe tip is introduced into the substrate vertically with a force introduced vertically upon the tip, while AFM introduces the tip vertically with a force introduced onto the tip and sample

via an essentially slightly inclined cantilever, however, each method for indentation can be used in the systems and methods according to the invention.

Existing methods utilizing nanoindentation or AFM based nanoindentation can, at present, estimate only various subsets of mechanical properties (*e.g.*, elastic modulus and hardness for elastic-plastic material models, or elastic modulus and viscosity for linear visco-elastic material models). Such limitations are present since current methods often involve steps in the loading or unloading procedures to simplify the analysis of the acquired load – displacement data by eliminating either plastic (time independent) or viscous (time dependent) components.

For complete characterization of polymers and polymer composites, it is important to know elastic, viscous, and plastic characteristics. In the case of composites, it is often necessary to resolve those properties on the nanoscale. Therefore, there exists a need to develop a process to determine viscous, elastic, and plastic properties, for example, elastic modulus, yield strain, complex modulus components as function of frequency, and the tip-sample work of adhesion, simultaneously. Quantitative nanomechanical measurements will greatly accelerate materials discovery and development by providing the tools and data to engineer materials tailored to handle specific stresses for specific applications, *i.e.*, materials by design.

## **SUMMARY OF THE INVENTION**

The current invention addresses the problems in existing methods by providing a testing procedure which allows for the simultaneous determination of viscous, elastic, and plastic properties of a material through combining the results of multiple nanoindentation tests and fitting the acquired data set according to nonlinear methods. The current invention also provides an associated analysis model for extracting the desired materials properties information from the data collected from the testing procedure.

In one aspect, the invention provides a method for determining properties of a sample via indentation testing, comprising: selecting a region of the sample where indentation will be performed; indenting the sample with an indenter tip using at least two locations, loading rates, and penetration depths, obtaining a load-displacement relationships from each indentation, and using the load-displacement relationships to determine at least two physical properties of the sample.

In another aspect, the invention provides a system comprising an indenter tip for indenting a sample, a controller for controlling indentation of the indenter tip against the sample and thereby obtaining a plurality of load-displacement relationships, wherein the plurality of load-displacement relationships represent multiple sample locations, multiple loading rates, and multiple penetration depths; and a data analysis system for determining at least two physical properties of the sample based on the plurality of load-displacement relationships.

The present invention enables a determination of elastic, viscous, plastic, and adhesive parameters of a material within the same test procedure. The inventive methods allow resolution of mechanical properties on a much smaller scale than conventional "bulk" testing (*e.g.*, AFM-based testing has resolution of about 100 nm, and conventional nanoindentation about 1000 nm).

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1(a) is a schematic representation of an exemplary setup.

Figure 1(b) is a typical load-displacement curve representative of AFM-based nanoindentation of a visco-elasto-plastic material.

Figure 1(c) is a schematic representation of a sequence of measurements that can be used to determine mechanical properties of materials as a function of loading rate and penetration depth ( $h_i$ ).

Figure 2 is a pictorial representation of a constitutive visco-elasto-plastic model used to analyze nanoindentation results.

Figure 3 is a scatter plot of  $(P/P_i)$  fitted (solid line) vs.  $(P/P_i)$  FEA data (points); trendline shows that the two sets are very close.

Figure 4(a) is FEA (symbols) and model fits (lines) of load-displacement relationship ( $P-h$ ) for small penetration depths and large and small loading rates.

Figure 4(b) is FEA (symbols) and model fits (lines) of load-displacement relationship ( $P-h$ ) for large penetration depths and large and small loading rates.

Figure 5 shows load-displacement curves for PMMA from nanoindentation.

Figure 6 shows calculated stress-strain curves for PMMA.

Figure 7 compares the modulus vs. strain rate of PMMA.

Figure 8 shows load-displacement curves for PC from nanoindentation.

Figure 9 shows calculated stress-strain curves for PC.

Figure 10 compares the modulus vs. strain rate of PC.

Figure 11 shows load-displacement curves for PS from nanoindentation.

Figure 12 shows calculated stress-strain curves for PS.

Figure 13 compares the modulus vs. strain rate of PS.

5 Figure 14 is a flow chart illustrating an embodiment of the method of the invention when the hysteresis of the second load-displacement relationship is less than or equal to a predetermined value, corresponding to predominately linear elastic behavior.

Figure 15 is a flow chart illustrating an embodiment of the method of the invention when the hysteresis of the second load-displacement relationship is greater than the  
10 predetermined value and the hysteresis of the third load-displacement relationship is less than or equal to a predetermined value, corresponding to predominately linear visco-elastic behavior.

Figure 16 is a flow chart illustrating an embodiment of the method of the invention when the hysteresis of the second load-displacement relationship is greater than the  
15 predetermined value and the hysteresis of the third load-displacement relationship is greater than a predetermined value, corresponding to predominately visco-elastic-plastic behavior.

## **DETAILED DESCRIPTION OF THE INVENTION**

20 In a first aspect, the invention provides a method for determining properties of a sample via indentation testing (*e.g.*, via AFM or nanoindentation), comprising the steps of:

- (i) selecting a region of the sample where indentation will be performed;
- (ii) indenting the sample with an indenter tip within the selected region, at  
25 more than one location,  
more than one loading rate,  
and more than one penetration depth, and  
obtaining a load-displacement relationship from each indentation; and
- (iii) using the load-displacement relationships to determine at least two physical  
30 properties of the sample,

such method is referred to hereafter as Method A.

In a first embodiment of the first aspect, the invention provides the method of Method A, wherein (ii) comprises the steps of,

indenting the sample with an indenter tip at a first location within the selected region at a first loading rate and a first penetration depth to obtain a first load-displacement relationship;

5 indenting the sample with an indenter tip at a second location within the selected region at a second loading rate and a second penetration depth to obtain a second load-displacement relationship, wherein

the first loading rate and the second loading rate are not identical, and analyzing the load-displacement relationship obtained from the greater of the first and second loading rates to determine at least one property of the material;

10 such method is referred to hereafter as Method B.

Accordingly, analysis of the load-displacement relationship determined from the greater of the first and second loading rates may be preformed after one or both of the first and second load-displacement relationships are collected.

In another embodiment of the first aspect, the invention provides the method of  
15 Method A, wherein (ii) comprises the steps of,

(a) indenting the sample with an indenter tip at a first location within the selected region at a first loading rate and a first penetration depth to obtain a first load-displacement relationship;

20 (b) analyzing the first load-displacement relationship to determine at least one property of the material; and

(c) indenting the sample with an indenter tip at a second location within the selected region at a second loading rate and a second penetration depth to obtain a second load-displacement relationship, wherein

the first loading rate is greater than the second loading rate,

25 such method is referred to hereafter as Method B-1.

In an alternative embodiment of the first aspect, the invention provides the method of Method A, wherein (ii) comprises the steps of,

30 (a) indenting the sample with an indenter tip at a first location within the selected region at a first loading rate and a first penetration depth to obtain a first load-displacement relationship;

(b) indenting the sample with an indenter tip at a second location within the selected region at a second loading rate and a second penetration depth to obtain a second load-displacement relationship, wherein

the first loading rate is greater than the second loading rate, and

(c) analyzing the first load-displacement relationship to determine at least one property of the material;

such method is referred to hereafter as Method B-2.

5 In an alternative embodiment of the first aspect, the invention provides the method of Method A, wherein (ii) comprises the steps of,

(a) indenting the sample with an indenter tip at a first location within the selected region at a first loading rate and a first penetration depth to obtain a first load-displacement relationship;

10 (b) indenting the sample with an indenter tip at a second location within the selected region at a second loading rate and a second penetration depth to obtain a second load-displacement relationship, wherein

the second loading rate is greater than the first loading rate, and

(c) analyzing the second load-displacement relationship to determine at least one property of the material;

15 such method is referred to hereafter as Method B-3.

In another embodiment of the first aspect, the invention provides the method of Method B, B-1, B-2, or B-3, wherein (ii) further comprises the step of,

(d) comparing the hysteresis of the second load-displacement relationship to a first predetermined value,

20 such method is referred to hereafter as Method C.

In another embodiment of the first aspect, the invention provides the method of Method C, wherein (ii) further comprises:

(e) indenting the sample with an indenter tip at a third location within the selected region at a third loading rate and a third penetration depth to obtain a third load-displacement relationship, wherein

the third loading rate is greater than the second loading rate; and

the third penetration depth is greater than both the first and second penetration depths,

30 such method is referred to hereafter as Method D.

In another embodiment of the first aspect, the invention provides the method of Method D, wherein when the hysteresis of the second load-displacement relationship is less than or equal to the first predetermined value, then no more indentations are made,

such method is referred to hereafter as Method E.

In another embodiment of the first aspect, the invention provides the method of Method D, wherein when the hysteresis of the second load-displacement relationship is greater than the first predetermined value, then (ii) further comprises:

- 5           (f) comparing the hysteresis of the third load-displacement relationship to a second predetermined value,

such method is referred to hereafter as Method F.

In another embodiment of the first aspect, the invention provides the method of Method F, wherein when the hysteresis of the third load-displacement relationship is less  
10   than or equal to the second predetermined value, then (ii) further comprises:

(g) indenting the sample with an indenter tip at a fourth location within the selected region at a fourth loading rate and a fourth penetration depth to obtain a fourth load-displacement relationship, wherein

- 15           the fourth loading rate is greater than the second loading rate and less than the first and third loading rates; and  
            the fourth penetration depth is greater than the first and second penetration depths and less than the third penetration depth,

such method is referred to hereafter as Method G.

In another embodiment of the first aspect, the invention provides the method of Method F, wherein when the hysteresis of the third load-displacement relationship is  
20   greater than the second predetermined value, then (ii) further comprises:

(g) indenting the sample with an indenter tip at a fourth location within the selected region at a fourth loading rate and a fourth penetration depth to obtain a fourth load-displacement relationship, wherein

- 25           the fourth loading rate is less than the first and third loading rates;  
            and  
            the fourth penetration depth is greater than both the first and second penetration depths;  
            and

- 30           (h) indenting the sample with an indenter tip at a fifth location within the selected region at a fifth loading rate and a fifth penetration depth to obtain a fifth load-displacement relationship, wherein

the fifth loading rate is greater than the second and fourth loading rates and less than the first and third loading rates; and

the fifth penetration depth is greater than the first and second penetration depths and less than the third and fifth penetration depths,

5 wherein the (g) and (h) may be performed in any order; such method is referred to hereafter as Method H. In a preferred embodiment, (g) is preformed before (h).

In a preferred embodiment of Methods C – H, the first and second predetermined values (*i.e.*, for maximum allowable hysteresis) are independently less than or equal to 0.10.

10 In a preferred embodiment of Methods A – H and B-1 – B-3, the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius, the first loading rate is about 1 nm/s to 100,000 nm/s, and the second loading rate is about 0.1 nm/s to 10,000 nm/s.

In a preferred embodiment of Methods D – H, wherein the third penetration depth is about 0.5 to 1.0 times the indenter tip radius, and the third loading rate is about 1 nm/s to 100,000 nm/s.

In a preferred embodiment of Method G, the fourth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and the fourth loading rate is about 0.3 nm/s to 30,000 nm/s.

20 In a preferred embodiment of Method H, the fourth penetration depth is about 0.5 to 1.0 times the indenter tip radius, the fourth loading rate is about 0.1 nm/s to 10,000 nm/s, the fifth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and the fifth loading rate is about 0.3 nm/s to 30,000 nm/s.

In a more preferred embodiment of Methods A – H and B-1 – B-3, the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius, the first and third loading rates are independently about 1 nm/s to 100,000 nm/s, the second loading rate is about 0.1 nm/s to 10,000 nm/s, and the third penetration depth is about about 0.5 to 1.0 times the indenter tip radius.

30 In a more preferred embodiment of Method G, the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius, the first and third loading rates are independently about 1 nm/s to 100,000 nm/s, the second loading rate is about 0.1 nm/s to 10,000 nm/s, the third penetration depth is about 0.5 to 1.0 times

the indenter tip radius, the fourth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and the fourth loading rate is about 0.3 nm/s to 30,000 nm/s.

In a more preferred embodiment of Method H, the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius, the first and third loading rates are independently about 1 nm/s to 100,000 nm/s, the second and fourth loading rates are independently about 0.1 nm/s to 10,000 nm/s, the third and fourth penetration depths are independently about 0.5 to 1.0 times the indenter tip radius, the fifth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and the fifth loading rate is about 0.3 nm/s to 30,000 nm/s.

Preferably, in (ii)(b) of any of the preceding embodiments, at least one physical property of the material determined is reduced modulus ( $E_r$ ) and/or work of adhesion ( $\gamma$ ) between the sample and indenter tip. More preferably, in (ii)(b) the at least one physical property of the material determined is reduced modulus ( $E_r$ ) and work of adhesion ( $\gamma$ ) between the sample and indenter tip.

Even more preferably, the at least one physical property of the material determined is reduced modulus ( $E_r$ ) and work of adhesion ( $\gamma$ ) between the sample and indenter tip, and the reduced modulus ( $E_r$ ) and work of adhesion ( $\gamma$ ) between the sample and indenter tip are determined from the slope and y-intercept, respectively, of the load-displacement relationship from (ii)(a) when load (P) is plotted as a function of  $h^{3/2}$  (e.g., Eq. 3, *vide infra*).

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the first and second locations coincide.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein each location within the region where the sample is indented is separated from any of the other indentation locations by a center-to-center distance of at least 5 times the highest of the penetration depths.

In a more preferred embodiment of Methods A – H and B-1 – B-3, when an AFM tip is used, then the first and second penetration depths are each independently about 5 nm to 10 nm, the first loading rate is about 1 nm/s to 100,000 nm/s, and the second loading rate is about 0.1 nm/s to 10,000 nm/s.

In a preferred embodiment of Methods D – H, when an AFM tip is used, then the third penetration depth is about 60 nm to 100 nm and the third loading rate is about 1 nm/s to 100,000 nm/s.

5 In a preferred embodiment of Method G, when an AFM tip is used, then the fourth penetration depth is about 20 nm to 40 nm and the fourth loading rate is about 0.3 nm/s to 30,000 nm/s.

10 In a preferred embodiment of Method H, when an AFM tip is used, then the fourth penetration depth is about 60 nm to 100 nm, the fourth loading rate is about 0.1 nm/s to 10,000 nm/s, the fifth penetration depth is about 20 nm to 40 nm, and the fifth loading rate is about 0.3 nm/s to 30,000 nm/s.

15 In a more preferred embodiment of Methods A – H and B-1 – B-3, when an AFM tip is used, then the first and second penetration depths are each independently about 5 nm to 10 nm, the first and third loading rates are independently about 1 nm/s to 100,000 nm/s, the second loading rate is about 0.1 nm/s to 10,000 nm/s, and the third penetration depth is about 60 nm to 100 nm.

20 In a more preferred embodiment of Method G, when an AFM tip is used, then the first and second penetration depths are each independently about 5 nm to 10 nm, the first and third loading rates are independently about 1 nm/s to 100,000 nm/s, the second loading rate is about 0.1 nm/s to 10,000 nm/s, the third penetration depth is about 60 nm to 100 nm, the fourth penetration depth is about 20 nm to 40 nm, and the fourth loading rate is about 0.3 nm/s to 30,000 nm/s.

25 In a more preferred embodiment of Method H, when an AFM tip is used, then the first and second penetration depths are each independently about 5 nm to 10 nm, the first and third loading rates are independently about 1 nm/s to 100,000 nm/s, the second and fourth loading rates are independently about 0.1 nm/s to 10,000 nm/s, the third and fourth penetration depths are independently about 60 nm to 100 nm, the fifth penetration depth is about 20 nm to 40 nm, and the fifth loading rate is about 0.3 nm/s to 30,000 nm/s.

30 In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the first and/or third loading rates are about 1 nm/s to about 100,000 nm/s.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the second and/or fourth loading rates are about 0.1 nm/s to about 10,000 nm/s.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the fifth loading rate is about 0.3 nm/s to about 30,000 nm/s.

5 In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the indenter tip comprises a material selected from the group consisting of silicon, silicon carbide, silicon nitride, diamond, sapphire, or silicon coated with silicon carbide, silicon nitride, diamond, and sapphire.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments wherein the indenter tip is spherical or parabolic.

10 In a preferred embodiment, the invention provides the method of any of the preceding embodiments wherein the indenter tip is spherical or parabolic and the indenter tip comprises a material selected from the group consisting of silicon, silicon carbide, silicon nitride, diamond, sapphire, or silicon coated with silicon carbide, silicon nitride, diamond, and sapphire.

15 In a preferred embodiment, the invention provides the method of any of the preceding embodiments wherein the indenter tip is spherical or parabolic and has a radius of about 10 to about 10,000 nm.

In a more preferred embodiment, the invention provides the method of any of the preceding embodiments wherein the indenter tip is a spherical or parabolic AFM tip and  
20 has a radius of about 5 to 200 nm; preferably, the radius is about 20 to about 50 nm.

In a more preferred embodiment, the invention provides the method of any of the preceding embodiments wherein the indenter tip is a spherical or parabolic conventional nanoindenter tip and has a radius of about 100 to 10,000 nm; preferably, the radius is 100 nm to 1000 nm.

25 In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the sample has a thickness of at least 10 times the highest penetration depth of all indentations performed. More preferably, the sample has a thickness of at least 20 times the highest penetration depth of all indentations performed.

In a preferred embodiment, the invention provides the method of any of the  
30 preceding embodiments, wherein at least two materials properties are selected from the group consisting of Young's modulus, work of adhesion, yield strain, viscosity, and relaxation time.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, further comprising the steps of non-dimensionalizing the obtained load-displacement relationship from each indentation by dividing the load data by the final load value for each indentation.

- 5 In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the load-displacement relationships are converted to effective stress—strain ( $\sigma$ — $\varepsilon$ ) curves via the transformation:

$$\sigma = \frac{P - P_{\min}}{\pi R^2}$$

10 
$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

wherein  $P$  is the load,  $P_{\min}$  is the minimum load ( $P_{\min} \leq 0$ ),  $h$  is penetration depth, and  $R$  is the radius of the indenter tip.

- 15 In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the reduced modulus, Young's modulus, relaxation time, and yield strength are obtained by fitting the effective stress-strain curves to a specific micromechanical model, such as Hookean, Maxwell, or Kelvin models.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein in (iii), the obtained load-displacement relationships are fit via non linear modeling to the model,

20 
$$\sigma = E_r \left[ v_M s \tau \left( 1 - \exp \left\{ -\frac{\varepsilon}{s \tau} \right\} \right) + v_H \left( X_e(\varepsilon) \varepsilon + [1 - X_e(\varepsilon)] \varepsilon_Y \left( 1 - \exp \left\{ \frac{\varepsilon}{\varepsilon_Y} \right\} \right) \right) \right],$$

wherein

$$X_e(\varepsilon) = \frac{1}{1 + C \left( \frac{\varepsilon}{\varepsilon_Y} \right)^{1/3}}; \quad s = D \frac{4}{3\pi t_{load}} \left[ \frac{h_t}{R} \right]^{3/2};$$

$$\varepsilon = (4/3\pi)(h/R)^{3/2}; \quad \sigma = (P - P_{\min})/\pi R^2 = (P + 2\pi\gamma R)/\pi R^2;$$

- 25  $v_M$  and  $v_H$  denote relative contributions of the Maxwellian and Hookean elements respectively, wherein  $v_M + v_H = 1$ ;

$R$  is the radius of the indenter tip;  $P$  is the measured load;  $h$  is the penetration depth;  $h_t$  is the final penetration depth;  $t_{load}$  is the total time for the indenter to

reach  $h_i$ ;  $E_r$  is the reduced modulus;  $\tau$  is relaxation time;  $\gamma$  is the work of adhesion between the indenter tip and sample;  $\varepsilon_y$  is yield strain; and C and D are empirically determined constants, and

the indenter tip is spherical or parabolic;

5 such method is referred to hereafter as Method I.

In another preferred embodiment, the invention provides the method of Method H, wherein the data are fit by optimizing via nonlinear modeling with respect to  $\tau$  and  $\varepsilon_y$ .

In another preferred embodiment, the invention provides the method of Method H, wherein the data are fit by optimizing via nonlinear modeling with respect to  $\tau$  and  $\varepsilon_y$ ,  
10 wherein  $\tau$  and  $\varepsilon_y$  are optimized by minimizing  $\chi^2$  between the measured data and the model.

In another preferred embodiment, the invention provides the method of Method H, wherein when the hysteresis in (ii)(d) is less than or equal to the predetermined value, then  $v_M = 0$  is used when fitting the data to the preceding model.

15 In another preferred embodiment, the invention provides the method of Method H, wherein when the hysteresis in (ii)(f) is less than or equal to the predetermined value, then  $\varepsilon_y = \infty$  is used when fitting the data to the preceding model.

In a preferred embodiment of any of the preceding embodiments, the predetermined value is 0.10. Preferably, the predetermined value is 0.05.

20 In a preferred embodiment of Methods A – I and B-1 – B-3, each of the penetration depths are predetermined.

In a preferred embodiment of Methods A – I and B-1 – B-3, each of the loading rates are predetermined.

In a more preferred embodiment of Methods A – I and B-1 – B-3, each of the  
25 penetration depths and loading rates are predetermined.

In a second aspect, the invention provides a system comprising:

an indenter tip for indenting a sample;

a controller for controlling indentation of the indenter tip against the sample and thereby obtaining a plurality of load-displacement relationships, wherein

30 the plurality of load-displacement relationships represent multiple sample locations, multiple loading rates, and multiple penetration depths; and  
a data analysis system for determining at least two physical properties of the sample based on the plurality of load-displacement relationships.

In a preferred embodiment of the second aspect, the controller is an atomic force microscope or nanoindenter.

In a preferred embodiment of the second aspect, the plurality of load-displacement relationships are collected according to the method of any embodiment of the first aspect.

5 In a more preferred embodiment of the second aspect, the controller is an atomic force microscope or nanoindenter and the plurality of load-displacement relationships are collected according to the method of any embodiment of the first aspect.

10 In an even more preferred embodiment of the second aspect, the controller is an atomic force microscope and the plurality of load-displacement relationships are collected according to the method of any embodiment of the first aspect.

In an even more preferred embodiment of the second aspect, the controller is an nanoindenter and the plurality of load-displacement relationships are collected according to the method of any embodiment of the first aspect.

15 In another preferred embodiment of the second aspect, the indenter tip comprises a material selected from the group consisting of silicon, silicon carbide, silicon nitride, diamond, sapphire, or silicon coated with silicon carbide, silicon nitride, diamond, and sapphire.

In another preferred embodiment of the second aspect, the indenter tip is spherical or parabolic and has a radius of about 10 to about 10,000 nm.

20 In a more preferred embodiment of the second aspect, the indenter tip is a spherical or parabolic AFM tip and has a radius of about 5 to 200 nm; preferably, the radius is about 20 to about 50 nm.

In a more preferred embodiment of the second aspect, the indenter tip is a spherical or parabolic conventional nanoindenter tip and has a radius of about 100 to 10,000 nm; preferably, the radius is 100 nm to 1000 nm.

25 In another preferred embodiment of the second aspect, the indenter tip comprises a material selected from the group consisting of silicon, silicon carbide, silicon nitride, diamond, sapphire, or silicon coated with silicon carbide, silicon nitride, diamond, and sapphire, and the indenter tip is spherical or parabolic and has a radius of about 10 to about 100 nm.

30 In another preferred embodiment of the second aspect, the data analysis system comprises a computer and software to analyze the obtained load-displacement relationships and thereby determine at least two materials properties of the sample.

In another preferred embodiment of the second aspect, the indenter tip is spherical or parabolic, and the data analysis includes a step wherein the load-displacement relationships are converted to effective stress—strain ( $\sigma$ — $\varepsilon$ ) curves via the transformation:

$$\sigma = \frac{P - P_{\min}}{\pi R^2}$$

$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

wherein  $P$  is the load,  $P_{\min}$  is the minimum load ( $P_{\min} \leq 0$ ),  $h$  is penetration depth, and  $R$  is the radius of the indenter tip.

In a preferred embodiment, the invention provides the method of any of the preceding embodiments, wherein the reduced modulus, Young's modulus, relaxation time, and yield strength are obtained by fitting the effective stress-strain curves to a specific micromechanical model, such as Hookean, Maxwell, or Kelvin models.

In another preferred embodiment of the second aspect, the indenter tip is spherical or parabolic, and the data analysis system determines at least two physical properties of the sample based on the plurality of load-displacement relationships by fitting the load-displacement relationships to the following model,

$$\sigma = E_r \left[ v_M s \tau \left( 1 - \exp \left\{ -\frac{\varepsilon}{s \tau} \right\} \right) + v_H \left( X_e(\varepsilon) \varepsilon + [1 - X_e(\varepsilon)] \varepsilon_Y \left( 1 - \exp \left\{ \frac{\varepsilon}{\varepsilon_Y} \right\} \right) \right) \right],$$

wherein

$$X_e(\varepsilon) = \frac{1}{1 + C \left( \frac{\varepsilon}{\varepsilon_Y} \right)^{1/3}}; \quad s = D \frac{4}{3\pi t_{load}} \left[ \frac{h_t}{R} \right]^{3/2};$$

$$\varepsilon = (4/3\pi)(h/R)^{3/2}; \quad \sigma = (P - P_{\min})/\pi R^2 = (P + 2\pi\gamma R)/\pi R^2;$$

$v_M$  and  $v_H$  denote relative contributions of the Maxwellian and Hookean elements respectively, wherein  $v_M + v_H = 1$ ;

$R$  is the radius of the indenter tip,  $P$  is the measured load,  $h$  is the penetration depth,  $h_t$  is the final penetration depth,  $t_{load}$  is the total time for the indenter to reach  $h_t$ ,  $E_r$  is the reduced modulus,  $\tau$  is relaxation time,  $\gamma$  is the work of

adhesion between the indenter tip and sample,  $\varepsilon_y$  is yield strain, and C and D are empirically determined constants).

### **Analysis Model**

5 The current invention is able to evaluate not only reduced modulus (as can be done using Oliver-Pharr [see Oliver and Pharr, *J. Mater. Res.* 7:1564; Oliver and Pharr, *J. Mater. Res.* 19:3 (2004)] or similar methods), but also relaxation time and yield strain. A suitable algorithm for the calculation is given below.

10 It is well-known that the load-displacement curve for the indentation of spherical tip into linear elastic material is described by Hertz' equation [see Sneddon, *Int. J. Eng. Sci.* 3:47 (1965); Hertz, *On the Contact of Two Elastic Solids*, MacMillan (1882)]:

$$P = \frac{4}{3} E_r R^{1/2} h^{3/2} \quad (1)$$

where  $P$  is load (in N),  $R$  is tip radius (in m),  $h$  is penetration depth (in m), and  $E_r$  is the reduced modulus of a sample, given by:

$$15 \quad E_r = \frac{E}{1 - \nu^2} \quad (2)$$

where  $E$  is Young's modulus of the sample (in Pa), and  $\nu$  is Poisson's ratio.

In deriving equation (1), the modulus of the indenter tip is much higher than the modulus of the sample. Hertz' equation is modified if there is adhesion between sample and tip. In the case of shallow, long-range tip- sample adhesive interactions, Derjaguin-  
20 Toporov-Muller (DMT) [see Maugis, *J. Colloid Interface Sci.* 150:243 (1992); Derjaguin *et al.*, *J. Colloid Interfacial Sci.* 53:314 (1975)] approximation can be used:

$$P = \frac{4}{3} E_r R^{1/2} h^{3/2} - 2\pi R \gamma \quad (3)$$

where  $\gamma$  (in N/m) is the work of adhesion. It is also known that in the case of linear viscoelastic material, load-displacement behavior can be approximated by the following  
25 expression (see Lee and Radok, *J. Appl. Mech.* 27:438 (1960)):

$$h^{3/2}(t) = \frac{3}{4R^{1/2}} \int_0^t J(t - \xi) \left[ \frac{dP(\xi)}{d\xi} \right] d\xi \quad (4)$$

where  $J(t)$  is compliance, defined so that  $J(t \rightarrow \infty) = 1/E_r$ . Note that equation (4) is applicable in the case of prescribed loading history (load-controlled indentation, rather than displacement-controlled indentation).

If one uses substitution  $\varepsilon = (4/3\pi)(h/R)^{3/2}$ ,  $\sigma = (P - P_{min})/\pi R^2 = (P + 2\pi\gamma R)/\pi R^2$ , it is possible to write an approximate solution for the dependence of  $\sigma$  on  $\varepsilon$  in a general elastic and viscoelastic case:

$$\sigma = E_r \left[ \nu_M (s\tau) \left[ 1 - \exp\left(-\frac{t}{\tau}\right) \right] + \nu_H s t \right] = E_r \left[ \nu_M (s\tau) \left[ 1 - \exp\left(-\frac{\varepsilon}{s\tau}\right) \right] + \nu_H \varepsilon \right] \quad (5)$$

5 Equation (5) is written for the simplest case of "minimal solid state model" or "one-element Prony series" (see, Lu *et al.*, *Mech. Time-Depend. Mater.* 7:189 (2003)), in which Maxwell element is connected in parallel with Hookean element;  $\nu_M$  and  $\nu_H$  denote relative contributions of two elements, with  $\nu_M + \nu_H = 1$ .

10 To describe plasticity, one can assume that the Hookean element is changed to elastic-perfectly plastic element. In that case, equation (5) is modified as follows:

$$\sigma = E_r \left[ \nu_M s \tau \left( 1 - \exp\left\{-\frac{\varepsilon}{s\tau}\right\} \right) + \nu_H \left( X_e(\varepsilon) \varepsilon + [1 - X_e(\varepsilon)] \varepsilon_Y \left( 1 - \exp\left\{\frac{\varepsilon}{\varepsilon_Y}\right\} \right) \right) \right] \quad (6)$$

where  $X_e(\varepsilon)$  describes the fraction of Hookean elements that remain elastic and not yielded at a given deformation  $\varepsilon$ . Approximate expression for  $X_e(\varepsilon)$  is given by:

$$X_e(\varepsilon) = \frac{1}{1 + C \left( \frac{\varepsilon}{\varepsilon_Y} \right)^{1/3}} \quad (7)$$

15 In experiment, the indentation is performed with constant indentation speed  $V = dh/dt = h_t/t_{load}$ . This indentation speed is related to the deformation rate  $s = d\varepsilon/dt$ , with the following relationship:

$$s = D \frac{\varepsilon_t}{t_{load}} = D \frac{4}{3\pi t_{load}} \left[ \frac{h_t}{R} \right]^{3/2} \quad (8)$$

20 Constants C and D are determined empirically. Equations (1) - (8) complete the set of equations needed to describe loading curves for arbitrary visco-elasto-plastic materials using spherical or parabolic indenters.

## **DEFINITIONS**

25 The term "penetration depth",  $h$ , as used herein, means the distance (with respect to the free surface) into a sample the indenter tip penetrates when a load is applied to the surface of the sample by the tip.

The term “loading rate” as used herein means the rate at which a conventional nanoindenter tip penetrates the surface of the sample or a AFM cantilever deflects when a load is applied by the tip; the load as a function of time applied to the sample by the tip is adjusted to maintain a constant loading rate.

5       The term “unloading rate” as used herein means the rate at which indenter tip is removed from a sample when the load applied by the tip is decreased; the load as a function of time applied to the sample by the tip is adjusted to maintain a constant unloading rate.

10       The term “hysteresis” as used herein, means the ratio of the area between the measured loading and unloading load-displacement relationships to the total area under the loading curve, restricted to the area where loads are positive.

15       The term “final load value”,  $P_t$ , as used herein, means the measured load applied to a sample by the indenter tip when the tip has reached the desired penetration depth for the measurement. The final load value is unique for each indentation depth and rate measurement and is used to non-dimensionalize the acquired data.

      The term “minimum load value”,  $P_{min}$ , as used herein, means the minimum value of the measured load applied to a sample by the indenter tip. This minimum can be zero (no adhesion) or a negative value (in the presence of adhesion).

20       The term reduced modulus,  $E_r$ , is defined as the ratio of Young’s modulus,  $E$ , to  $(1 - \nu^2)$  where  $\nu$  is the Poisson ratio, provided that the indenter modulus is significantly higher than the sample modulus.

      The term  $\chi^2$  as used herein means the total sum of the least squares of the deviations of the observed data points from the model as defined herein (*supra*).

25       The term “load-displacement relationship” as used herein, means the relationship obtained from the loading and unloading of a sample with an indenter tip; each load-displacement relationship defines an associated hysteresis, as defined herein.

30       Herein, the radius of a parabolic indenter tip is the radius of curvature of the portion of the indenter tip which is placed in contact with a sample. For a tip of arbitrary shape, the radius is that of the closest parabolic tip. The closest parabolic tip is defined as the tip of parabolic shape whose cross-sectional view is the closest to that of the current tip.

## **EXAMPLES**

### *Example 1- Finite Element Analysis - Simulated Nanoindentation Test of a Visco-elasto-plastic Model Material*

5

In the following example, the software package, ABAQUS/Standard (Providence, RI, USA; Version 6.5-7), is used to generate load-indentation curves. The terms '\*VISCOUS', '\*ELASTIC', and '\*PLASTIC' are material behavior descriptors within the software package.

10

We use Finite Element Analysis (FEA) computer modeling software to simulate load-indentation curves. For FEA simulation, ABAQUS/Standard (Providence, RI, USA; Version 6.5-7) is used. Indenter tip is represented as a hard sphere with radius  $R = 100$  nm. Indented material is modeled as a visco-elasto-plastic half-space, with Young's modulus  $E = 2.69$  GPa, Poisson's ratio  $\nu = 0.35$ , yield strain  $\epsilon_y = 0.05$ , and relaxation time  $\tau = 50$  sec. A visco-elastoplastic model of an element used to represent the material is shown in Figure 2.

15

The following assumptions are used in the simulation: (a) perfectly smooth surfaces; (b) frictionless contact; (c) homogenous visco-elastic-plastic half-space; (d) 20 adhesion less contact interface. The spherical indenter is modeled using a 2-D analytical rigid surface. The half-space is modeled with axisymmetric 4-node bi-linear and 4-node bi-linear reduced integration solid elements. In order to simulate the contact area accurately, a very fine mesh of fully-integrated elements is used in a small region below the indenter. The mesh grows coarser away from the indenter in four stages; reduced- 25 integration elements are used in these regions. Infinite axisymmetric elements are used to model far-field regions of the half-space. Nodes on the boundary  $x = 0$  (excluding those belonging to the infinite element) are constrained against displacement in the x-direction. No boundary conditions need to be enforced on the edges of the infinite elements in the infinite directions. Contact between the indenter and half-space is modeled as frictionless 30 contact using the default contact pressure-clearance relationship in ABAQUS referred to as the "hard" contact model.

Viscoplastic material behavior is modeled using the two-layer viscoplasticity approach which uses the '\*VISCOUS' option together with the '\*ELASTIC' and '\*PLASTIC'

options. The load-unload test cycle is simulated by applying prescribed displacements to the indenter reference node in two nonlinear steps. In each step, a \*VISCO procedure is used to conduct a quasi-static analysis with transient response to time-dependent material behavior. In the first step, a prescribed displacement equal to the desired maximum penetration is applied to displace the indenter downward. In the second step, a prescribed displacement of zero is applied causing the indenter to return to its original position.

Five simulations are performed: (1) loading time,  $T_t = 2$  sec, penetration depth,  $h_t = 5$  nm; (2)  $T_t = 200$  sec,  $h_t = 5$  nm; (3)  $T_t = 20$  sec,  $h_t = 30$  nm; (4)  $T_t = 2$  sec,  $h_t = 60$  nm; and (5)  $T_t = 200$  sec,  $h_t = 60$  nm. Load-penetration curves are generated for all five cases.

Data fitting (determination of visco-elasto-plastic parameters of the material) is performed as follows: take the loading curve from the case (1), convert load-displacement ( $P - h$ ) to stress-strain ( $\sigma - \epsilon$ ) and perform linear fit using Microsoft Excel (with the option of setting intercept = 0). The slope of the fit gives reduced modulus  $E_r = 3.10$  GPa (vs. exact value of 3.066 GPa). To determine other two parameters, relaxation time  $\tau$ , and yield strain  $\epsilon_y$ , all five loading curves are non-dimensionalized by dividing  $P$  by  $P_t$ . All non-dimensional loads are then imported into statistical analysis software JMP 6.0; "nonlinear" modeling feature is used to fit the non-dimensional loads by optimizing with respect to parameters  $\tau$  and  $\epsilon_y$ .

Fit results are shown in Figures 3 and 4, showing that the model and FEA data are very close to each other. Fit parameters are summarized in Table 1, together with the exact values (input FEA parameters). For reduced modulus we also provide the estimate from the incumbent method (Oliver-Pharr) to show that the new procedure provides equal or better accuracy.

| Material Parameter | Exact Values | Model Calculations for Fitting | Oliver-Pharr |
|--------------------|--------------|--------------------------------|--------------|
| $E_r$ (GPa)        | 3.066        | 3.1                            | 2.97         |
| $\tau$ (sec.)      | 50           | 55                             |              |
| $\epsilon_y$       | 0.05         | 0.049                          |              |
|                    |              |                                |              |

**Table 1.** Calculated values of reduced modulus, relaxation time, and yield strain (third column) compared to exact values (second column). For comparison purposes, an Oliver-Pharr estimate of the reduced modulus is given in the fourth column (the Oliver-Pharr method does not provide estimates for the other two material parameters).

*Example 2 – PMMA Nanoindentation*

Polymethylmethacrylate (PMMA) is obtained in sheet form (2mm thick) from Goodfellow Cambridge Limited, Huntingdon, England (part number ME303020). This PMMA is a Repsol YPF acrylic with  $M_w = 1,810,000$  g/mol and  $M_n = 261,000$  g/mol, as may be measured by size exclusion chromatography using a linear polystyrene calibration.

Sample Preparation and Bulk Tensile Testing

Tensile specimens are cut from the 2mm sheet into 2.5 inch long and 0.25 inch wide bars using a high speed circular saw. Tensile tests are performed on an Instron 4201 with the Instron Bluehill software. The specimens are attached using Instron air grips pressurized to 80 psi. An Instron mechanical extensometer of one inch gauge length is reset to zero and attached to the specimen prior to testing to measure the tensile strain. Tensile tests are performed at 0.05, 0.5 and 5 mm/s.

Sample Preparation for Nanoindentation

Pieces of the PMMA sheet are cut by hand using a jeweler's saw. The pieces are embedded and cured in Buehler Epoxicure resin and hardener inside 1.25 inch diameter forms for metallographic polishing. Polishing is obtained using a Struers Rotopol and following a sequence of five grinding steps all at 70N applied force:

- i) 1200 grit SiC paper using DI water lubricant for 20 sec;
- ii) 2400 grit SiC paper using DI water lubricant for 10 sec;
- iii) 4000 grit Sic paper using DI water lubricant for 10 sec;
- iv) 3 micron diamond in Texmet cloth using Leco diamond paste extender lubricant for 3 min;
- v) 0.25 micron diamond in Texmet cloth using Leco diamond paste with extender lubricant for 4 min.

Final polish is obtained on a Buehler Vibromet using 0.25  $\mu$ m diamond on a LeCloth surface with Leco diamond paste extender lubricant for 2 hours under 300 gms load.

#### Nanoindentation testing - constant strain rate

Nanoindentation experiments are performed on a MTS Nanoindenter (MTS Nano Instruments, Oak Ridge, TN) equipped with a DCM head and a Berkovich diamond Accutip indenter. The area function of the indenter tip is calibrated with fused silica by the manufacturer. The test is computer controlled through MTS Testworks software using a Continuous Stiffness Measurement (CSM) method that provides accurate detection of the surface of the indented materials. The CSM parameters are set at a frequency of 75Hz and amplitude of 1 nm. The detection of the surface is triggered by an increase of the harmonic contact stiffness higher than 100 N/m. The strain rate target of the loading curve is set at 0.05/s and the constant unloading rate is between 0.7 and 0.8 mN/s. Conventional Oliver-Pharr calculations [see Oliver and Pharr, *J. Mater. Res.* 7:1564; Oliver and Pharr, *J. Mater. Res.* 19:3 (2004)] of reduced modulus,  $E_r$ , and hardness,  $H$ , are automatically performed by the Testworks software with the Poisson ratio set at 0.35 and the portion of the unloading curve used for the automatic calculation set at 50%.

#### Nanoindentation testing - constant displacement rate experiments

The nanoindentation experiments are performed on a MTS DCM nanoindenter equipped with a DCM head and a Berkovich diamond Accutip indenter. The area function of the indenter tip is calibrated with fused silica by the manufacturer. The test is computer controlled through MTS Testworks software using a Continuous Stiffness Measurement (CSM) method that provides accurate detection of the surface of the indented materials. The CSM parameters are set at a frequency of 75Hz and amplitude of 1 nm. The detection of the surface is triggered by an increase of the harmonic contact stiffness higher than 100 N/m. The standard MTS Testworks CSM method is modified by replacing the constant strain rate criterion with a constant displacement rate criterion in the method. Load-displacement curves data are exported using the export function of the Testworks software for visco-elastic-plastic-adhesive analysis.

Load-displacement curves for PMMA are plotted in Figure 5. Five displacement-controlled loading-unloading measurements are shown, with maximum penetration depth and average speed for each run summarized in Table 2. Because of the substantial hysteresis between the curves corresponding to different indentation speeds, the material is determined to possess viscous, elastic, and plastic characteristics.

| Label     | $h_{\max}$ , nm | $P_{\max}$ , mN | $v$ , nm/sec | $s$ , $\text{sec}^{-1}$ |
|-----------|-----------------|-----------------|--------------|-------------------------|
| High-High | 136.57          | 0.18            | 86.00        | 2.18E-01                |
| High-Low  | 101.97          | 0.07            | 2.10         | 5.00E-03                |
| Med-Med   | 65.40           | 0.04            | 36.00        | 4.80E-02                |
| Low-High  | 21.88           | 0.012           | 59.00        | 5.30E-02                |
| Low-Low   | 11.91           | 0.0039          | 3.40         | 2.00E-03                |

Table 2. Nanoindentation measurement parameters. Here,  $h_{\max}$  is the maximum penetration,  $P_{\max}$  is the maximum load,  $v$  is the indentation speed, and  $s$  is the average rate of change of the deformation variable  $\varepsilon$ .

To analyze the data and estimate visco-elasto-plastic properties of the polymer, it is useful to transform the (P—h) description to the ( $\sigma$ — $\varepsilon$ ) description, according to:

$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

$$\sigma = \frac{P}{\pi R^2}$$

The load-displacement curves in the new coordinates (stress-strain) are plotted in Figure 6. The effective reduced modulus,  $E_r$ , for each deformation rate (High, Medium, and Low) is calculated by fitting the loading portion of the  $\sigma$ — $\varepsilon$  curve with a straight line. The results are summarized in Table 3. (Reduced modulus is converted to Young's modulus via the standard expression,  $E = E_r(1 - \nu^2)$ , where Poisson's ratio is taken as  $\nu = 0.35$ ). For comparison purposes, bulk tensile measurements may be taken at various strain rates on the same polymer. In Figure 7, calculated modulus and measured bulk modulus are plotted as function of effective strain rate  $s$ ; it can be seen that the results are in a good agreement.

| Label     | s, sec <sup>-1</sup> | Er, GPa | E, GPa |
|-----------|----------------------|---------|--------|
| High-High | 2.18E-01             | 6.53    | 5.73   |
| Med-Med   | 4.80E-02             | 3.86    | 3.39   |
| High-Low  | 5.00E-03             | 5.30    | 4.65   |

Table 3. Calculated reduced modulus and Young's modulus as function of the average strain rate  $s$ .

Viscoelastic effects are manifested in the dependence of the modulus on the deformation rate. To approximately evaluate the characteristic relaxation time,  $\tau$ , the dependence of  $E$  (or, to be more precise, compliance  $E^{-1}$ ) on  $s$  may be fitted to the following function:

$$E^{-1}(s) = J_0 + J_1 \exp(-s \tau)$$

The values of  $J_0$ ,  $J_1$ , and  $\tau$  are summarized in Table 4.

| $J_0$ , GPa <sup>-1</sup> | $J_1$ , GPa <sup>-1</sup> | $\tau$ , sec |
|---------------------------|---------------------------|--------------|
| 0.174                     | 0.13                      | 25           |

Table 4. Calculated compliance parameters and characteristic relaxation time.

To analyze plastic properties of PMMA such as yield stress or yield strain, it is useful to consider both the loading and unloading portions of the curve. For the case of High-Low measurement, a measure of plasticity,  $H$ , may be defined as:

$$H = E_r(s) \{ \varepsilon_t - \varepsilon_f \}$$

Here,  $\varepsilon_t$  is the maximum deformation, and  $\varepsilon_f$  is the final deformation (related to the plasticity of the material). The higher is  $H$ , the more "elastic" is the behavior of the material (for a given  $\varepsilon_t$ ). In particular, one can associate  $H$  with the stress at which the plastic deformation begins, i.e., hardness of the material. Then, yield stress  $\sigma_Y$  can be

evaluated based on the Tabor formula [see D. Tabor, *The Hardness and Strength of Metals*, Oxford Clarendon Press, 1951] (with Tabor constant  $k \approx 2.9$ ):

$$H = k\sigma_Y$$

Calculated values of  $H$  and  $\sigma_Y$  are given in Table 5.

| H, GPa | $\sigma_Y$ , GPa |
|--------|------------------|
| 0.5    | 0.172            |

Table 5. Calculated hardness and yield stress for PMMA.

Typical literature values of yield stress for PMMA range from 50 to 150 MPa, so the estimate given by this method is slightly higher than expected value. The discrepancy probably could be ascribed to strain hardening in compression.

The standard Oliver-Pharr analysis yields the following estimates for  $E_r$ ,  $E$ ,  $H$ , and  $\sigma_y$ :  $E_r = 5.46$  GPa;  $E = 4.79$  GPa;  $H = 0.31$  GPa;  $\sigma_y = 0.107$  GPa.

### *Example 3 – PC Nanoindentation*

Polycarbonate (PC) is obtained in sheet form (2mm thick) from Goodfellow Cambridge Limited, Huntingdon, England (part number CT303100). This is a Bayer Makrolon type PC with  $M_w = 49,000$  g/mol and  $M_n = 13,000$  g/mol, as may be measured by size exclusion chromatography using a linear polystyrene calibration.

#### Sample Preparation and Bulk Tensile Testing

Tensile specimens are cut from the 2mm sheet into 2.5 inch long and 0.25 inch wide bars using a high speed circular saw. Tensile tests are performed on an Instron 4201 with the Instron Bluehill software. The specimens are attached using Instron air grips pressurized to 80 psi. An Instron mechanical extensometer of one inch gauge length is reset to zero

and attached to the specimen prior to testing to measure the tensile strain. Tensile tests are performed at 0.05, 0.5 and 5 mm/s.

Pieces of the PC sheet are cut by hand using a jeweler's saw. The pieces are embedded and cured in Buehler Epoxicure resin and hardener inside 1.25 inch diameter forms for metallographic polishing. Polishing is obtained using a Struers Rotapol and following a sequence of five grinding steps all at 70N applied force:

- i) 1200 grit SiC paper using DI water lubricant for 20 sec;
- ii) 2400 grit SiC paper using DI water lubricant for 10 sec;
- iii) 4000 grit Sic paper using DI water lubricant for 10 sec;
- iv) 3 micron diamond in Texmet cloth using Leco diamond paste extender lubricant for 3 min;
- v) 0.25 micron diamond in Texmet cloth using Leco diamond paste with extender lubricant for 4 min.

Final polish is obtained on a Buehler Vibromet using 0.25 um diamond on a LeCloth surface with Leco diamond paste extender lubricant for 2 hours under 300 gms load.

#### Nanoindentation testing - constant strain rate

Nanoindentation experiments are performed on a MTS Nanoindenter (MTS Nano Instruments, Oak Ridge, TN) equipped with a DCM head and a Berkovich diamond Accutip indenter. The area function of the indenter tip is calibrated with fused silica by the manufacturer. The test is computer controlled through MTS Testworks software using a Continuous Stiffness Measurement (CSM) method that provides accurate detection of the surface of the indented materials. The CSM parameters are set at a frequency of 75Hz and amplitude of 1 nm. The detection of the surface is triggered by an increase of the harmonic contact stiffness higher than 100 N/m. The strain rate target of the loading curve is set at 0.05/s and the constant unloading rate is between 0.7 and 0.8 mN/s.

Conventional Oliver-Pharr calculations [see Oliver and Pharr, *J. Mater. Res.* 7:1564; Oliver and Pharr, *J. Mater. Res.* 19:3 (2004)] of reduced modulus,  $E_r$ , and hardness,  $H$ , are automatically performed by the Testworks software with the Poisson ratio set at 0.35 and the portion of the unloading curve used for the automatic calculation set at 50%.

### Nanoindentation testing - constant displacement rate experiments

The nanoindentation experiments are performed on a MTS DCM nanoindenter equipped with a DCM head and a Berkovich diamond Accutip indenter. The area function of the indenter tip is calibrated with fused silica by the manufacturer. The test is computer controlled through MTS Testworks software using a Continuous Stiffness Measurement (CSM) method that provides accurate detection of the surface of the indented materials. The CSM parameters are set at a frequency of 75Hz and amplitude of 1 nm. The detection of the surface is triggered by an increase of the harmonic contact stiffness higher than 100 N/m. The standard MTS Testworks CSM method is modified by replacing the constant strain rate criterion with a constant displacement rate criterion in the method. Load-displacement curves data are exported using the export function of the Testworks software for visco-elastic-plastic-adhesive analysis.

Load-displacement curves for PC are plotted in Figure 8. Five displacement-controlled loading-unloading measurements are shown, with maximum penetration depth and average speed for each run summarized in Table 6. Because of the substantial hysteresis between the curves corresponding to different indentation speeds, the material is determined to possess viscous, elastic, and plastic characteristics.

| Label     | $h_{\max}$ , nm | $P_{\max}$ , mN | $v$ , nm/sec | $s$ , $\text{sec}^{-1}$ |
|-----------|-----------------|-----------------|--------------|-------------------------|
| High-High | 134.16          | 0.0992          | 100.48       | 2.25E-01                |
| High-Low  | 101.23          | 0.0444          | 2.65         | 5.20E-03                |
| Med-Med   | 58.51           | 0.0255          | 39.25        | 5.76E-02                |
| Low-High  | 21.88           | 0.0119          | 96.59        | 1.10E-01                |
| Low-Low   | 12.14           | 0.0025          | 4.32         | 2.90E-03                |

Table 6. Nanoindentation measurement parameters. Here,  $h_{\max}$  is the maximum penetration,  $P_{\max}$  is the maximum load,  $v$  is the indentation speed, and  $s$  is the average rate of change of the deformation variable  $\varepsilon$ .

To analyze the data and estimate visco-elasto-plastic properties of the polymer, it is useful to transform the (P—h) description to the ( $\sigma$ — $\varepsilon$ ) description, according to:

$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

$$\sigma = \frac{P}{\pi R^2}$$

The load-displacement curves in the new coordinates (stress-strain) are plotted in Figure 9. The effective reduced modulus,  $E_r$ , for each deformation rate (High, Medium, and Low) is calculated by fitting the loading portion of the  $\sigma$ — $\varepsilon$  curve with a straight line. The results are summarized in Table 7. (Reduced modulus is converted to Young's modulus via the standard expression,  $E = E_r(1 - \nu^2)$ , where Poisson's ratio is taken as  $\nu = 0.35$ ). For comparison purposes, bulk tensile measurements may be taken at various strain rates on the same polymer. In Figure 10, calculated modulus and measured bulk modulus are plotted as function of effective strain rate  $s$ ; it can be seen that the results are in a good agreement.

| Label     | s, sec <sup>-1</sup> | $E_r$ , GPa | E, GPa |
|-----------|----------------------|-------------|--------|
| High-High | 2.25E-01             | 3.72        | 3.27   |
| Med-Med   | 5.76E-02             | 3.64        | 3.19   |
| High-Low  | 5.20E-03             | 2.35        | 2.06   |

Table 7. Calculated reduced modulus and Young's modulus as function of the average strain rate  $s$ .

Viscoelastic effects are manifested in the dependence of the modulus on the deformation rate. To approximately evaluate the characteristic relaxation time,  $\tau$ , the dependence of  $E$  (or, to be more precise, compliance  $E^{-1}$ ) on  $s$  may be fitted to the following function:

$$E^{-1}(s) = J_0 + J_1 \exp(-s \tau)$$

The values of  $J_0$ ,  $J_1$ , and  $\tau$  are summarized in Table 8.

| $J_0$ , GPa <sup>-1</sup> | $J_1$ , GPa <sup>-1</sup> | $\tau$ , sec |
|---------------------------|---------------------------|--------------|
| 0.3                       | 0.25                      | 50           |

Table 8. Calculated compliance parameters and characteristic relaxation time.

To analyze plastic properties of PC such as yield stress or yield strain, it is useful to consider both the loading and unloading portions of the curve. For the case of High-Low measurement, a measure of plasticity,  $H$ , may be defined as:

$$H = E_r(s) \{ \varepsilon_t - \varepsilon_f \}$$

Here,  $\varepsilon_t$  is the maximum deformation, and  $\varepsilon_f$  is the final deformation (related to the plasticity of the material). The higher is  $H$ , the more “elastic” is the behavior of the material (for a given  $\varepsilon_t$ ). In particular, one can associate  $H$  with the stress at which the plastic deformation begins, i.e., hardness of the material. Then, yield stress  $\sigma_Y$  can be evaluated based on the Tabor formula [ see D. Tabor, *The Hardness and Strength of Metals*, Oxford Clarendon Press, 1951] (with Tabor constant  $k \approx 2.9$ ):

$$H = k \sigma_Y$$

Calculated values of  $H$  and  $\sigma_Y$  are given in Table 9.

| $H$ , GPa | $\sigma_Y$ , GPa |
|-----------|------------------|
| 0.2       | 0.069            |

Table 9. Calculated hardness and yield stress for PC.

The results are in good agreement with manufacturer specifications for bulk tensile values for polycarbonate at room temperature ( $\sigma_y = 0.06\text{--}0.07$  GPa,  $E = 2.3\text{--}2.4$  GPa).

The standard Oliver-Pharr analysis yields the following estimates for  $E_r$ ,  $E$ ,  $H$ , and  $\sigma_y$ :  $E_r = 3.90$  GPa;  $E = 3.42$  GPa;  $H = 0.21$  GPa;  $\sigma_y = 0.072$  GPa.

#### *Example 4 – PS Nanoindentation*

Polystyrene (PS) is obtained in extruded pellet form from The Dow Chemical Company, Midland, MI (PS 1683). This PS is a general purpose atactic type with  $M_w = 269,000$  g/mol and  $M_n = 96,300$  g/mol, as may be measured by size exclusion chromatography using a linear polystyrene calibration.

#### Sample Preparation and Bulk Tensile Testing

Tensile specimens are prepared by compression molding at 255°C using the following sequence: 7mins at 1,000 psi for melting; 7mins at 40,000 psi for molding; and 40 mins slow cooling to room temperature. Tensile specimens are cut from molded forms into 2.5 inch long and 0.25 inch wide bars using a high speed circular saw. Tensile tests are performed on an Instron 4201 with the Instron Bluehill software. The specimens are attached using Instron air grips pressurized to 80 psi. An Instron mechanical extensometer of one inch gauge length is reset to zero and attached to the specimen prior to testing to measure the tensile strain. Tensile tests are performed at 0.05, 0.5 and 5 mm/s.

PS pellets are embedded and cured in Buehler Epoxicure resin and hardener inside 1.25 inch diameter forms for metallographic polishing. Polishing is obtained using a Struers Rotapol and following a sequence of five grinding steps all at 70N applied force:

- i) 1200 grit SiC paper using DI water lubricant for 20 sec;
- ii) 2400 grit SiC paper using DI water lubricant for 10 sec;
- iii) 4000 grit SiC paper using DI water lubricant for 10 sec;
- iv) 3 micron diamond in Texmet cloth using Leco diamond paste extender lubricant for 3 min;

v) 0.25 micron diamond in Texmet cloth using Leco diamond paste with extender lubricant for 4 min.

Final polish is obtained on a Buehler Vibromet using 0.25  $\mu\text{m}$  diamond on a LeCloth surface with Leco diamond paste extender lubricant for 2 hours under 300 gms load.

#### Nanoindentation testing - constant strain rate

Nanoindentation experiments were performed on a MTS Nanoindenter (MTS Nano Instruments, Oak Ridge, TN) equipped with a DCM head and a Berkovich diamond Accutip indenter. The area function of the indenter tip is calibrated with fused silica by the manufacturer. The test is computer controlled through MTS Testworks software using a Continuous Stiffness Measurement (CSM) method that provides accurate detection of the surface of the indented materials. The CSM parameters are set at a frequency of 75Hz and amplitude of 1 nm. The detection of the surface is triggered by an increase of the harmonic contact stiffness higher than 100 N/m. The strain rate target of the loading curve is set at 0.05/s and the constant unloading rate is between 0.7 and 0.8 mN/s.

Conventional Oliver-Pharr calculations [see Oliver and Pharr, *J. Mater. Res.* 7:1564; Oliver and Pharr, *J. Mater. Res.* 19:3 (2004)] of reduced modulus,  $E_r$ , and hardness,  $H$ , are automatically performed by the Testworks software with the Poisson ratio set at 0.35 and the portion of the unloading curve used for the automatic calculation set at 50%.

#### Nanoindentation testing - constant displacement rate experiments

The nanoindentation experiments are performed on a MTS DCM nanoindenter equipped with a DCM head and a Berkovich diamond Accutip indenter. The area function of the indenter tip is calibrated with fused silica by the manufacturer. The test is computer controlled through MTS Testworks software using a Continuous Stiffness Measurement (CSM) method that provides accurate detection of the surface of the indented materials. The CSM parameters are set at a frequency of 75Hz and amplitude of 1 nm. The detection of the surface is triggered by an increase of the harmonic contact stiffness higher than 100 N/m. The standard MTS Testworks CSM method is modified by replacing the constant strain rate criterion with a constant displacement rate criterion in the method. Load-displacement curves data are exported using the export function of the Testworks software for visco-elastic-plastic-adhesive analysis.

Load-displacement curves for PS are plotted in Figure 11. Five displacement-controlled loading-unloading measurements are shown, with maximum penetration depth and average speed for each run summarized in Table 10. Because of the substantial hysteresis between the curves corresponding to different indentation speeds, the material is determined to possess viscous, elastic, and plastic characteristics.

| Label     | $h_{\max}$ , nm | $P_{\max}$ , mN | $v$ , nm/sec | $s$ , $\text{sec}^{-1}$ |
|-----------|-----------------|-----------------|--------------|-------------------------|
| High-High | 121.79          | 0.13            | 94.13        | 2.07E-01                |
| High-Low  | 102.84          | 0.07            | 2.59         | 5.10E-03                |
| Med-Med   | 59.82           | 0.03            | 29.62        | 4.60E-02                |
| Low-High  | 24.71           | 0.013           | 76.48        | 7.45E-02                |
| Low-Low   | 11.82           | 0.0028          | 3.94         | 2.60E-03                |

Table 10. Nanoindentation measurement parameters. Here,  $h_{\max}$  is the maximum penetration,  $P_{\max}$  is the maximum load,  $v$  is the indentation speed, and  $s$  is the average rate of change of the deformation variable  $\varepsilon$ .

To analyze the data and estimate visco-elasto-plastic properties of the polymer, it is useful to transform the (P—h) description to the ( $\sigma$ — $\varepsilon$ ) description, according to:

$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

$$\sigma = \frac{P}{\pi R^2}$$

The load-displacement curves in the new coordinates (stress-strain) are plotted in Figure 12. The effective reduced modulus,  $E_r$ , for each deformation rate (High, Medium, and Low) is calculated by fitting the loading portion of the  $\sigma$ — $\varepsilon$  curve with a straight line. The results are summarized in Table 11. (Reduced modulus is converted to Young's modulus via the standard expression,  $E = E_r(1 - \nu^2)$ , where Poisson's ratio is taken as  $\nu = 0.35$ ). For comparison purposes, bulk tensile measurements may be taken at

various strain rates on the same polymer. In Figure 13, calculated modulus and measured bulk modulus are plotted as function of effective strain rate  $s$ ; it can be seen that the results are in a good agreement.

| Label     | $s, \text{sec}^{-1}$ | $E_r, \text{GPa}$ | $E, \text{GPa}$ |
|-----------|----------------------|-------------------|-----------------|
| High-High | 2.07E-01             | 5.50              | 4.83            |
| Med-Med   | 4.60E-02             | 4.34              | 3.81            |
| High-Low  | 5.10E-03             | 3.59              | 3.15            |

Table 11. Calculated reduced modulus and Young's modulus as function of the average strain rate  $s$ .

Viscoelastic effects are manifested in the dependence of the modulus on the deformation rate. To approximately evaluate the characteristic relaxation time,  $\tau$ , the dependence of  $E$  (or, to be more precise, compliance  $E^{-1}$ ) on  $s$  may be fitted to the following function:

$$E^{-1}(s) = J_0 + J_1 \exp(-s \tau)$$

The values of  $J_0$ ,  $J_1$ , and  $\tau$  are summarized in Table 12.

| $J_0, \text{GPa}^{-1}$ | $J_1, \text{GPa}^{-1}$ | $\tau, \text{sec}$ |
|------------------------|------------------------|--------------------|
| 0.2                    | 0.13                   | 15                 |

Table 12. Calculated compliance parameters and characteristic relaxation time.

To analyze plastic properties of PS such as yield stress or yield strain, it is useful to consider both the loading and unloading portions of the curve. For the case of High-Low measurement, a measure of plasticity,  $H$ , may be defined as:

$$H = E_r(s) \{ \varepsilon_t - \varepsilon_f \}$$

Here,  $\varepsilon_i$  is the maximum deformation, and  $\varepsilon_f$  is the final deformation (related to the plasticity of the material). The higher is  $H$ , the more “elastic” is the behavior of the material (for a given  $\varepsilon_i$ ). In particular, one can associate  $H$  with the stress at which the plastic deformation begins, i.e., hardness of the material. Then, yield stress  $\sigma_Y$  can be evaluated based on the Tabor formula [see D. Tabor, *The Hardness and Strength of Metals*, Oxford Clarendon Press, 1951] (with Tabor constant  $k \approx 2.9$ ):

$$H = k\sigma_Y$$

Calculated values of  $H$  and  $\sigma_Y$  are given in Table 13. The estimate of yield strain is based on the assumption that material can be considered visco-elastic-plastic. In the case of PS, brittle fracture is known to pre-empt plasticity so the observed hardness in bulk testing may be lower than the estimate obtained from nanoindentation.

| H, GPa | $\sigma_Y$ , GPa |
|--------|------------------|
| 0.45   | 0.155            |

Table 13. Calculated hardness and yield stress for PS.

The standard Oliver-Pharr analysis yields the following estimates for  $E_r$ ,  $E$ ,  $H$ , and  $\sigma_y$ :  $E_r = 5.13$  GPa;  $E = 4.50$  GPa;  $H = 0.25$  GPa;  $\sigma_y = 0.085$  GPa.

### **Conclusion**

It is to be understood that the foregoing examples are intended to be illustrative, rather than exhaustive, of the materials that may be studied and the procedures that may be used. Similar procedures may be used to characterize the viscous, elastic, and/or plastic properties of other materials.

We Claim:

1. A method for determining properties of a sample via indentation testing, comprising the steps of:
  - (i) selecting a region of the sample where indentation will be performed;
  - (ii) indenting the sample with an indenter tip within the selected region, at  
more than one location,  
more than one loading rate,  
and more than one penetration depth,  
to obtain a plurality of load-displacement relationships ;  
and
  - (iii) using the load-displacement relationships to determine at least two physical properties of the sample.
2. The method of claim 1, wherein (ii) comprises the steps of,  
indenting the sample with an indenter tip at a first location within the selected region at a first loading rate and a first penetration depth to obtain a first load-displacement relationship;  
indenting the sample with an indenter tip at a second location within the selected region at a second loading rate and a second penetration depth to obtain a second load-displacement relationship, wherein  
the first loading rate and the second loading rate are not identical, and  
analyzing the load-displacement relationship obtained from the greater of the first and second loading rates to determine at least one property of the material.
3. The method of claim 2, wherein (ii) comprises the steps of,
  - (a) indenting the sample with an indenter tip at a first location within the selected region at a first loading rate and a first penetration depth to obtain a first load-displacement relationship;
  - (b) analyzing the first load-displacement relationship to determine at least one property of the material; and

- (c) indenting the sample with an indenter tip at a second location within the selected region at a second loading rate and a second penetration depth to obtain a second load-displacement relationship, wherein
- the first loading rate is greater than the second loading rate.
4. The method of claim 3, wherein (ii) further comprises the step of,
- (d) comparing the hysteresis of the second load-displacement relationship to a first predetermined value.
5. The method of claim 4, wherein (ii) further comprises:
- (e) indenting the sample with an indenter tip at a third location within the selected region at a third loading rate and a third penetration depth to obtain a third load-displacement relationship, wherein
- the third loading rate is greater than the second loading rate;
- and
- the third penetration depth is greater than both the first and second penetration depths.
6. The method of claim 5, wherein
- when the hysteresis of the second load-displacement relationship is less than or equal to the first predetermined value, then no more indentations are made.
7. The method of claim 5, wherein
- when the hysteresis of the second load-displacement relationship is greater than the first predetermined value, then (ii) further comprises:
- (f) comparing the hysteresis of the third load-displacement relationship to a second predetermined value.
8. The method of claim 7, wherein when the hysteresis of the third load-displacement relationship is less than or equal to the second predetermined value, then (ii) further comprises:
- (g) indenting the sample with an indenter tip at a fourth location within the selected region at a fourth loading rate and a fourth penetration depth to obtain a fourth load-displacement relationship, wherein
- the fourth loading rate is greater than the second loading rate and less than the first and third loading rates;
- and

the fourth penetration depth is greater than the first and second penetration depths and less than the third penetration depth.

9. The method of claim 7, wherein when the hysteresis of the third load-displacement relationship is greater than the second predetermined value, then (ii) further comprises:
  - (g) indenting the sample with an indenter tip at a fourth location within the selected region at a fourth loading rate and a fourth penetration depth to obtain a fourth load-displacement relationship, wherein
    - the fourth loading rate is less than the first and third loading rates;
    - and
    - the fourth penetration depth is greater than both the first and second penetration depths;
    - and
  - (h) indenting the sample with an indenter tip at a fifth location within the selected region at a fifth loading rate and a fifth penetration depth to obtain a fifth load-displacement relationship, wherein
    - the fifth loading rate is greater than the second and fourth loading rates and less than the first and third loading rates;
    - and
    - the fifth penetration depth is greater than the first and second penetration depths and less than the third and fifth penetration depths,wherein the (g) and (h) may be performed in any order.
10. The method of any one of claims 2 – 9, wherein
  - the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius,
  - the first loading rate is about 1 nm/s to 100,000 nm/s, and
  - the second loading rate is about 0.1 nm/s to 10,000 nm/s.
11. The method of any one of claims 5 – 9, wherein
  - the third penetration depth is about 0.5 to 1.0 times the indenter tip radius, and
  - the third loading rate is about 1 nm/s to 100,000 nm/s.
12. The method of claim 8, wherein
  - the fourth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and
  - the fourth loading rate is about 0.3 nm/s to 30,000 nm/s.

13. The method of claim 9, wherein  
the fourth penetration depth is about 0.5 to 1.0 times the indenter tip radius,  
the fourth loading rate is about 0.1 nm/s to 10,000 nm/s,  
the fifth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and  
the fifth loading rate is about 0.3 nm/s to 30,000 nm/s.
14. The method of any one of claims 5 – 9, wherein  
the first and second penetration depths are each independently selected to be about 0.01 to 0.1 times the indenter tip radius,  
the first and third loading rates are independently about 1 nm/s to 100,000 nm/s,  
the second loading rate is about 0.1 nm/s to 10,000 nm/s, and  
the third penetration depth is about 0.5 to 1.0 times the indenter tip radius.
15. The method of claim 8, wherein  
the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius,  
the first and third loading rates are independently about 1 nm/s to 100,000 nm/s,  
the second loading rate is about 0.1 nm/s to 10,000 nm/s,  
the third penetration depth is about 0.5 to 1.0 times the indenter tip radius,  
the fourth penetration depth is about 0.2 to 0.5 times the indenter tip radius, and  
the fourth loading rate is about 0.3 nm/s to 30,000 nm/s.
16. The method of claim 9, wherein  
the first and second penetration depths are each independently about 0.01 to 0.1 times the indenter tip radius,  
the first and third loading rates are independently about 1 nm/s to 100,000 nm/s,  
the second and fourth loading rates independently about 0.1 nm/s to 10,000 nm/s,  
the third and fourth penetration depths are independently about r about 0.5 to 1.0 times the indenter tip radius,  
the fifth penetration depth is about about 0.2 to 0.5 times the indenter tip radius,  
and  
the fifth loading rate is about 0.3 nm/s to 30,000 nm/s.
17. The method of any one of claims 2 - 9, wherein the first and second locations coincide.
18. The method of any one of claims 1 - 9, wherein

each location within the region where the sample is indented is separated from any of the other indentation locations by a center-to-center distance of at least 5 times the highest of the penetration depths.

19. The method of any one of claims 1 - 9, wherein the indenter tip comprises a material selected from the group consisting of silicon, silicon carbide, silicon nitride, diamond, sapphire, or silicon coated with silicon carbide, silicon nitride, diamond, and sapphire.
20. The method of any one of claims 1 - 9, wherein the indenter tip is spherical or parabolic and has a radius of about 5 to about 200 nm.
21. The method of any one of claims 1 - 9, wherein the sample has a thickness of at least 10 times the highest penetration depth.
22. The method of any one of claims 1 - 9, wherein the at least two physical properties are selected from the group consisting of Young's modulus, work of adhesion, yield strain, viscosity, and relaxation time.
23. The method of any one of claims 1 - 9, wherein the load-displacement relationships are converted to effective stress—strain ( $\sigma$ — $\varepsilon$ ) curves via the transformation

$$\sigma = \frac{P - P_{\min}}{\pi R^2}$$

$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

wherein  $P$  is the load,  $P_{\min}$  is the minimum load ( $P_{\min} \leq 0$ ),  $h$  is penetration depth, and  $R$  is the radius of the indenter tip.

24. The method of any one of claims 1 - 9, wherein at least one of reduced modulus, Young's modulus, relaxation time, and yield strength are obtained by fitting the effective stress-strain curves to a micromechanical model.
25. The method of any one of claims 1 - 9, wherein the indenter tip is spherical or parabolic, and

(iii) comprises fitting the obtained load-displacement relationships to the following model,

$$\sigma = E_r \left[ v_M s \tau \left( 1 - \exp \left\{ -\frac{\varepsilon}{s \tau} \right\} \right) + v_H \left( X_e(\varepsilon) \varepsilon + [1 - X_e(\varepsilon)] \varepsilon_Y \left( 1 - \exp \left\{ \frac{\varepsilon}{\varepsilon_Y} \right\} \right) \right) \right],$$

wherein

$$X_e(\varepsilon) = \frac{1}{1 + C \left( \frac{\varepsilon}{\varepsilon_Y} \right)^{1/3}}; \quad s = D \frac{4}{3\pi t_{load}} \left[ \frac{h_t}{R} \right]^{3/2};$$

$$\varepsilon = (4/3\pi)(h/R)^{3/2}; \quad \sigma = (P - P_{min})/\pi R^2 = (P + 2\pi\gamma R)/\pi R^2;$$

$v_M$  and  $v_H$  denote relative contributions of the Maxwellian and Hookean elements respectively, wherein  $v_M + v_H = 1$ ;

$R$  is the radius of the indenter tip,  $P$  is the measured load,  $h$  is the penetration depth,  $h_t$  is the final penetration depth,  $t_{load}$  is the total time for the indenter to reach  $h_t$ ,  $E_r$  is the reduced modulus,  $\tau$  is relaxation time,  $\gamma$  is the work of adhesion between the indenter tip and sample,  $\varepsilon_Y$  is yield strain, and  $C$  and  $D$  are empirically determined constants.

26. The method of claim 25, wherein when the hysteresis in (ii)(c) is less than or equal to the predetermined value, then  $v_M = 0$  is used when fitting the data.
27. The method of claim 25, wherein when the hysteresis in (ii)(d) is less than or equal to the predetermined value, then  $\varepsilon_Y = \infty$  is used when fitting the data.
28. A system comprising:
  - an indenter tip for indenting a sample;
  - a controller for controlling indentation of the indenter tip against the sample capable of obtaining a plurality of load-displacement relationships, wherein
    - the plurality of load-displacement relationships represents multiple sample locations, multiple loading rates, and multiple penetration depths; and
  - a data analysis system for determining at least two physical properties of the sample based on the plurality of load-displacement relationships.
29. The system of claim 28, wherein the plurality of load-displacement relationships are collected according to the method of any one of claims 1 – 9.
30. The system of claim 28, wherein the indenter tip comprises a material selected from the group consisting of silicon, silicon carbide, silicon nitride, diamond,

sapphire, or silicon coated with silicon carbide, silicon nitride, diamond, and sapphire.

31. The system of claim 28 or 30, wherein the indenter tip is spherical or parabolic and has a radius of about 5 to about 200 nm.
32. The system of claim 29, wherein the indenter tip is spherical or parabolic, and the data analysis system is configured to convert the load-displacement relationships to effective stress—strain ( $\sigma$ — $\varepsilon$ ) curves via the transformation

$$\sigma = \frac{P - P_{\min}}{\pi R^2}$$

$$\varepsilon = \frac{4}{3\pi} \left( \frac{h}{R} \right)^{3/2}$$

wherein  $P$  is the load,  $P_{\min}$  is the minimum load ( $P_{\min} \leq 0$ ),  $h$  is penetration depth, and  $R$  is the radius of the indenter tip.

33. The system of claim 29, wherein the indenter tip is spherical or parabolic, and the data analysis system is configured to calculate at least one of Young's modulus, relaxation time, and yield strength by fitting the effective stress-strain curves to a micromechanical model.

34. The system of claim 29, wherein the indenter tip is spherical or parabolic, and the data analysis system determines at least two physical properties of the sample based on the plurality of load-displacement relationships by fitting the load-displacement relationships to the following model,

$$\sigma = E_r \left[ \nu_M s \tau \left( 1 - \exp \left\{ -\frac{\varepsilon}{s \tau} \right\} \right) + \nu_H \left( X_e(\varepsilon) \varepsilon + [1 - X_e(\varepsilon)] \varepsilon_Y \left( 1 - \exp \left\{ \frac{\varepsilon}{\varepsilon_Y} \right\} \right) \right) \right],$$

wherein

$$X_e(\varepsilon) = \frac{1}{1 + C \left( \frac{\varepsilon}{\varepsilon_Y} \right)^{1/3}}; \quad s = D \frac{4}{3\pi \tau_{load}} \left[ \frac{h_t}{R} \right]^{3/2};$$

$$\varepsilon = (4/3\pi)(h/R)^{3/2}; \quad \sigma = (P - P_{\min})/\pi R^2 = (P + 2\pi\gamma R)/\pi R^2;$$

$v_M$  and  $v_H$  denote relative contributions of the Maxwellian and Hookean elements respectively, wherein  $v_M + v_H = 1$ ;

$R$  is the radius of the indenter tip,  $P$  is the measured load,  $h$  is the penetration depth,  $h_t$  is the final penetration depth,  $t_{load}$  is the total time for the indenter to reach  $h_t$ ,  $E_r$  is the reduced modulus,  $\tau$  is relaxation time,  $\gamma$  is the work of adhesion between the indenter tip and sample,  $\varepsilon_y$  is yield strain, and  $C$  and  $D$  are empirically determined constants.

35. The system of claim 34, wherein the at least two physical properties are selected from the group consisting of Young's modulus, work of adhesion, yield strain, viscosity, and relaxation time.

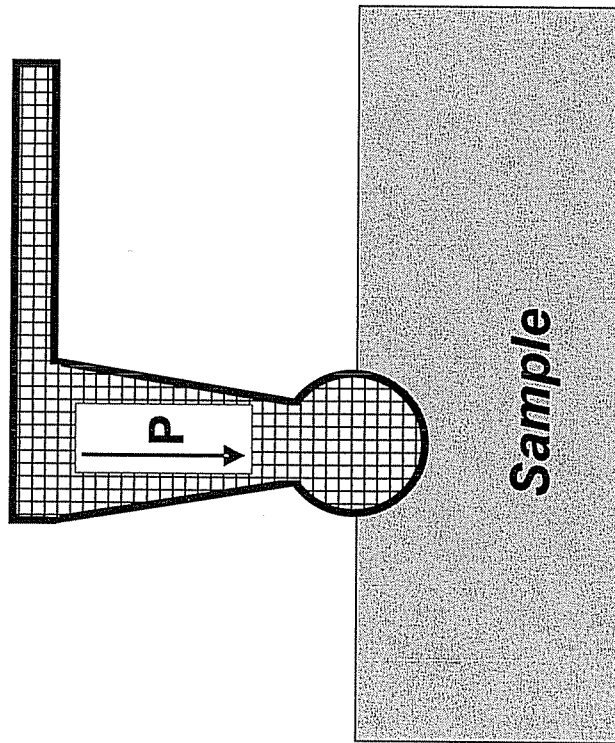


Figure 1a

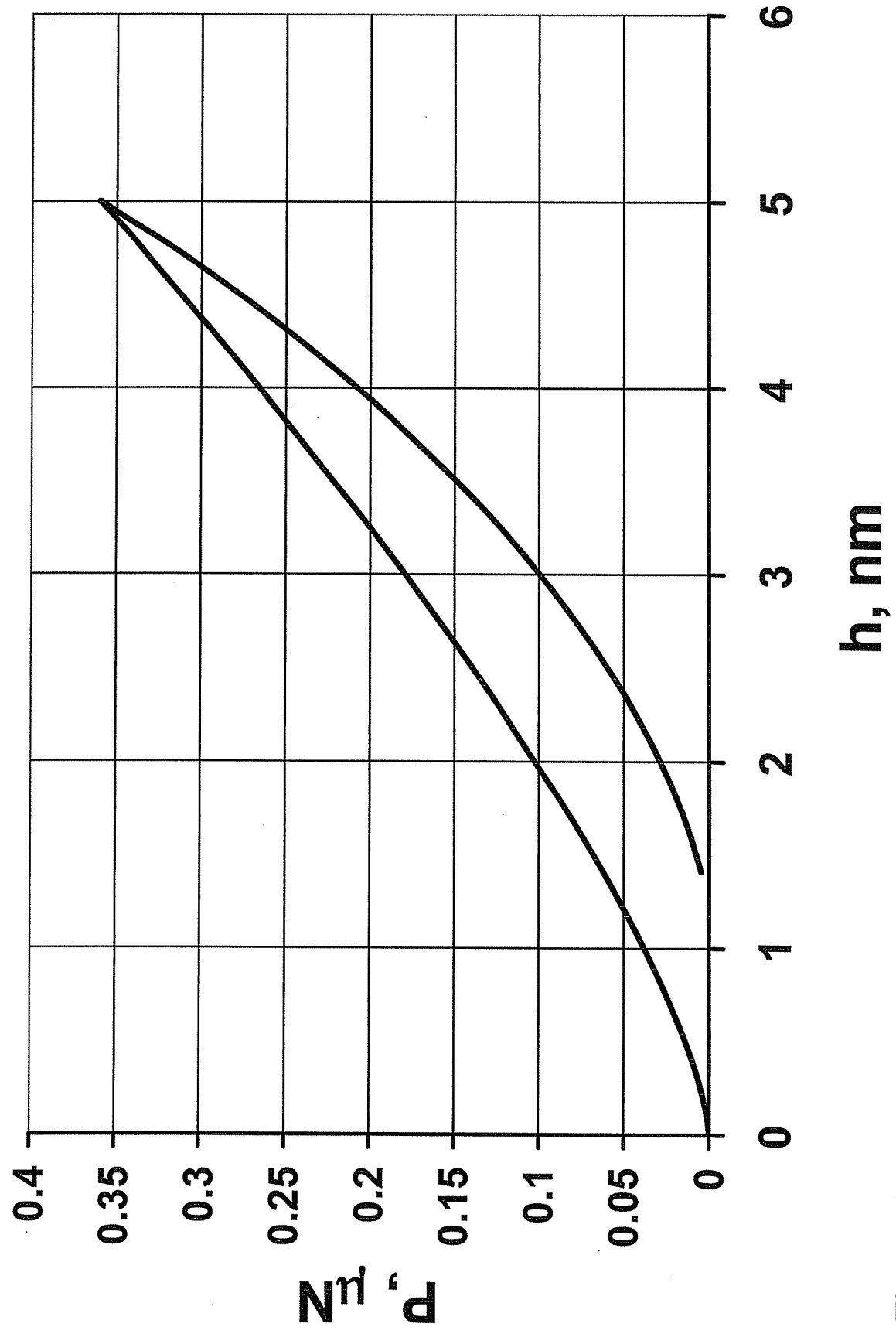


Figure 1b

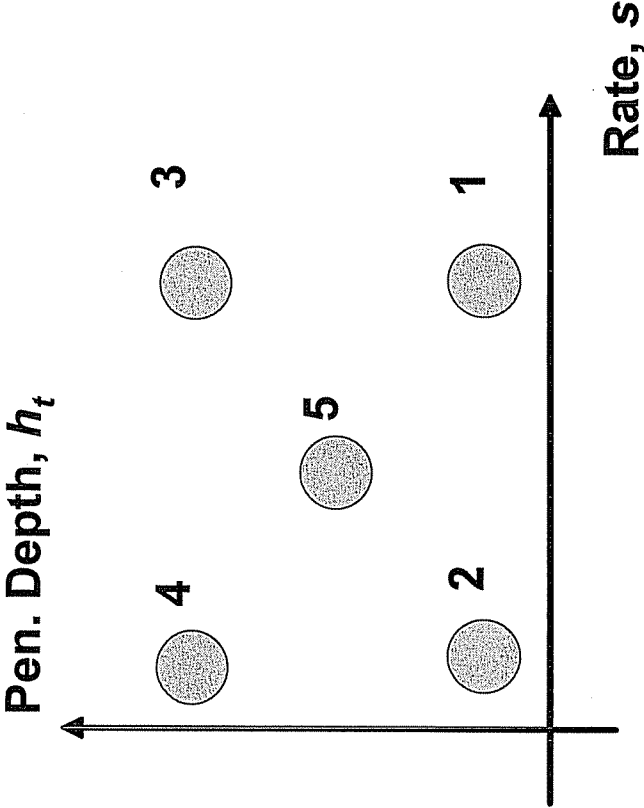


Figure 1c

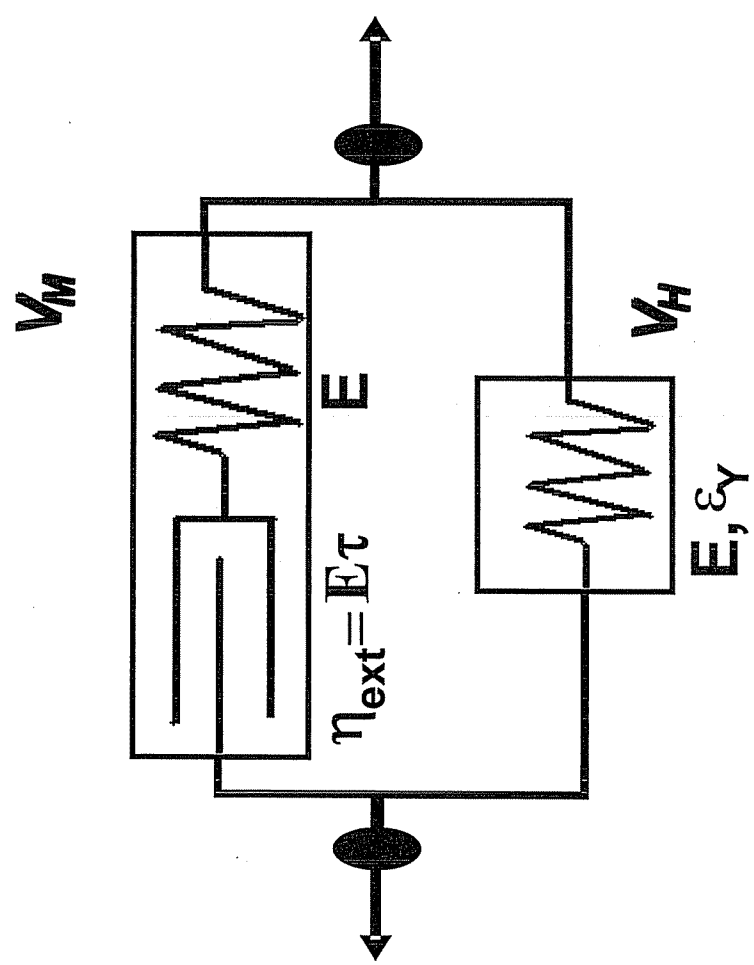


Figure 2

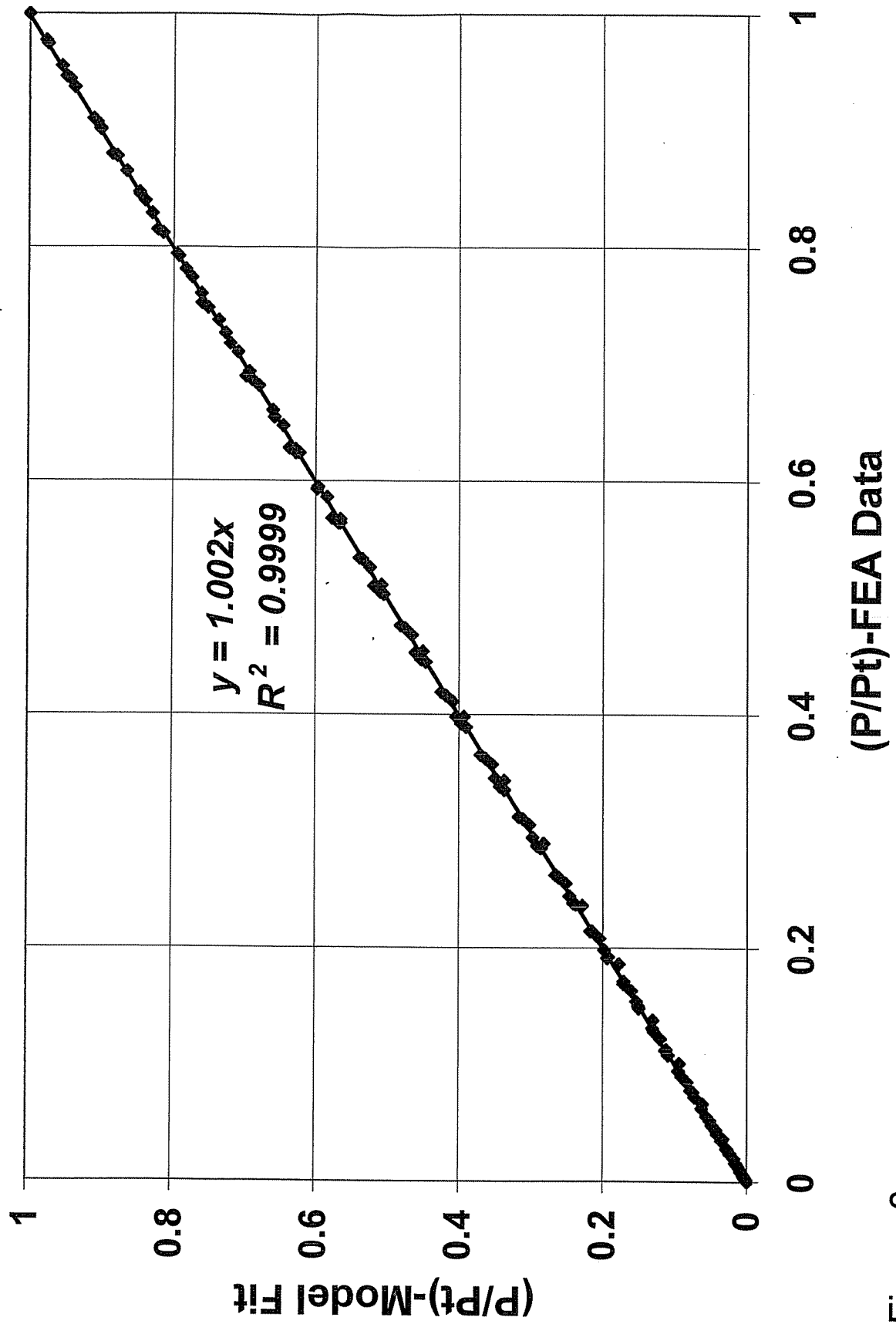


Figure 3

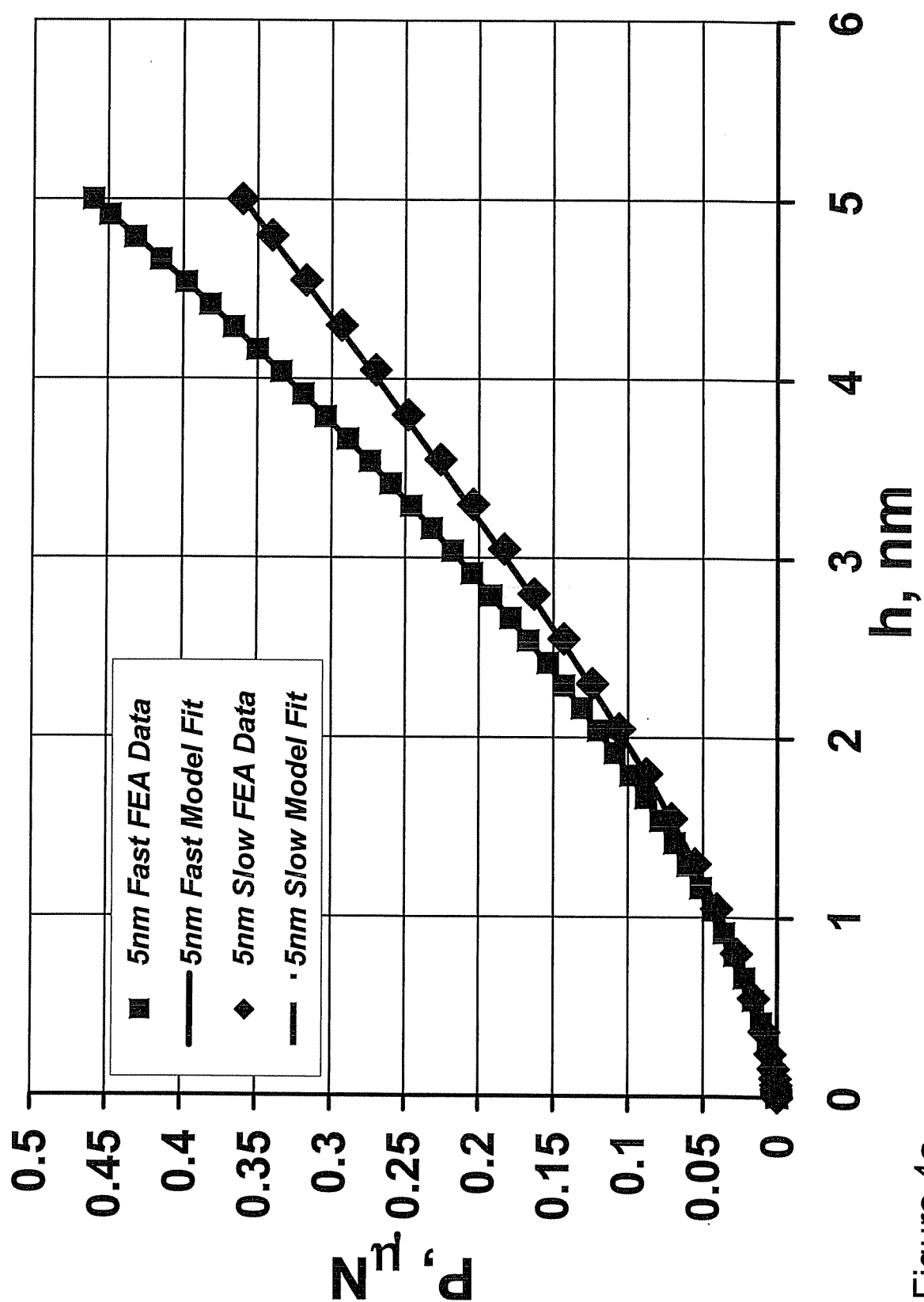


Figure 4a

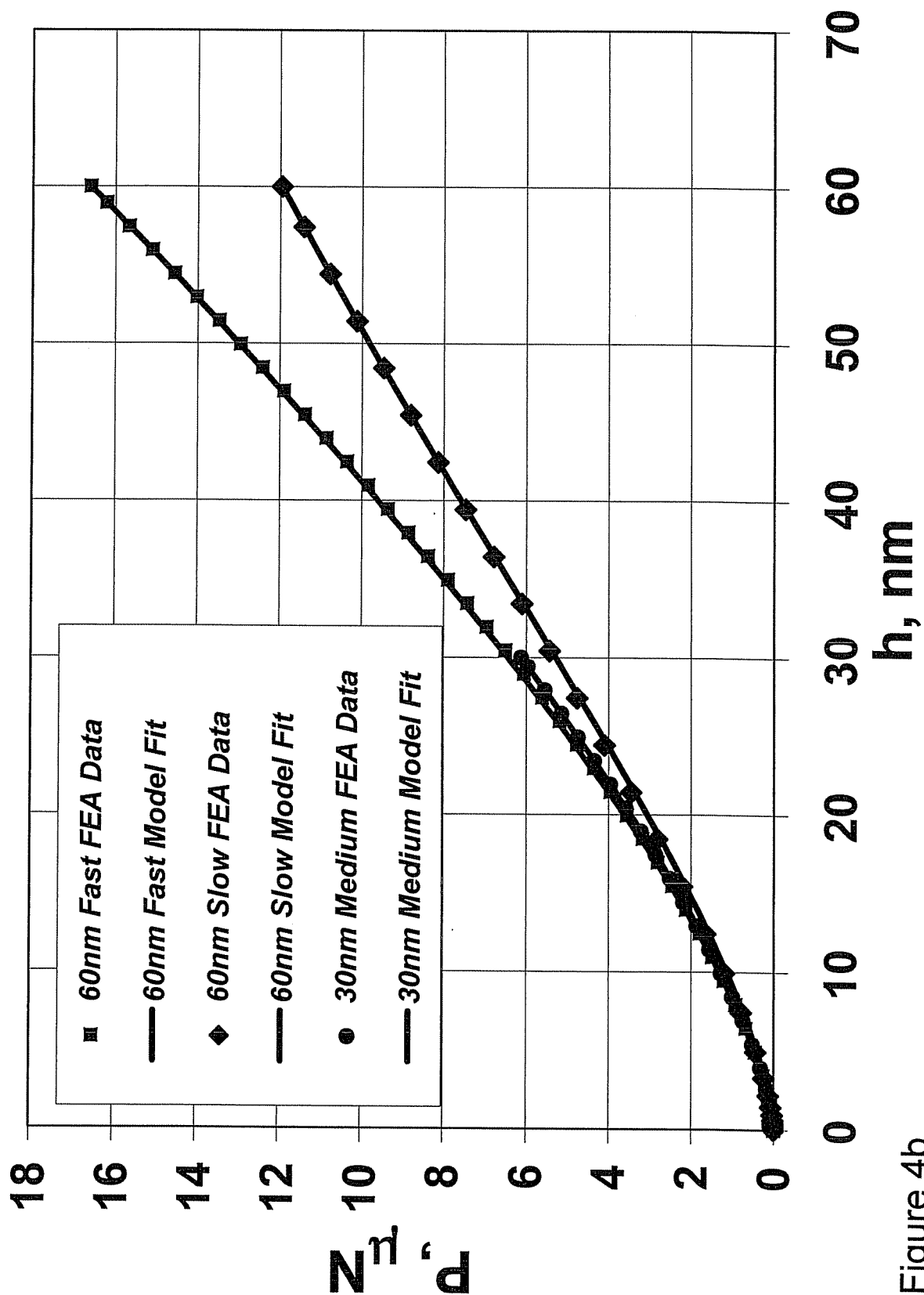


Figure 4b

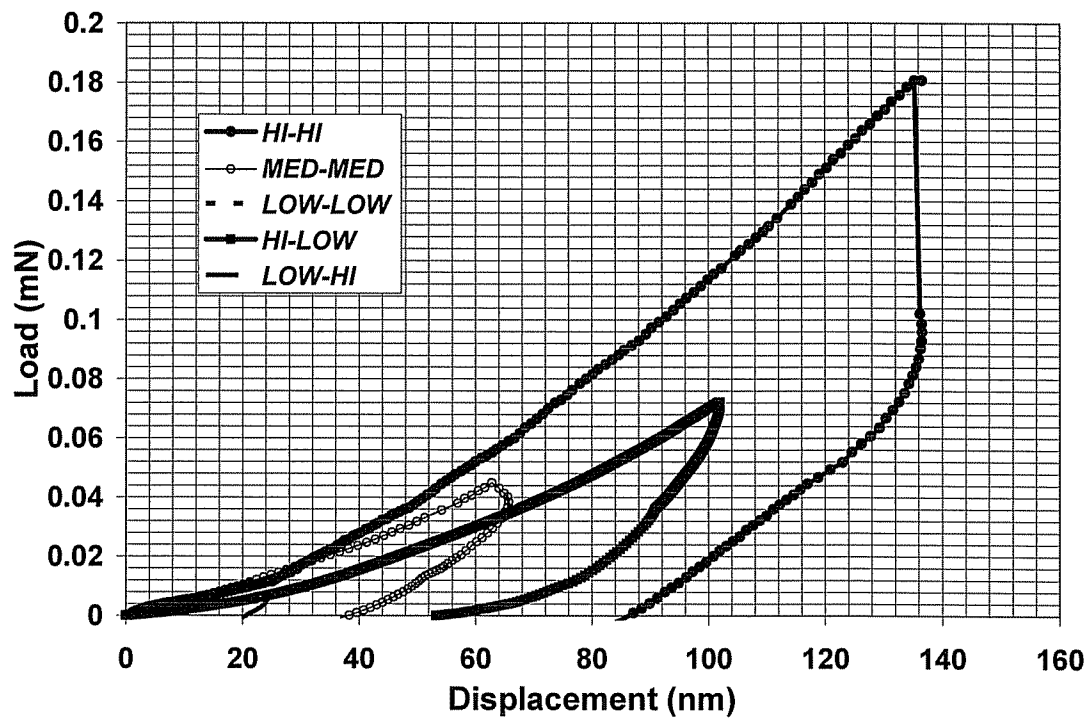


Figure 5

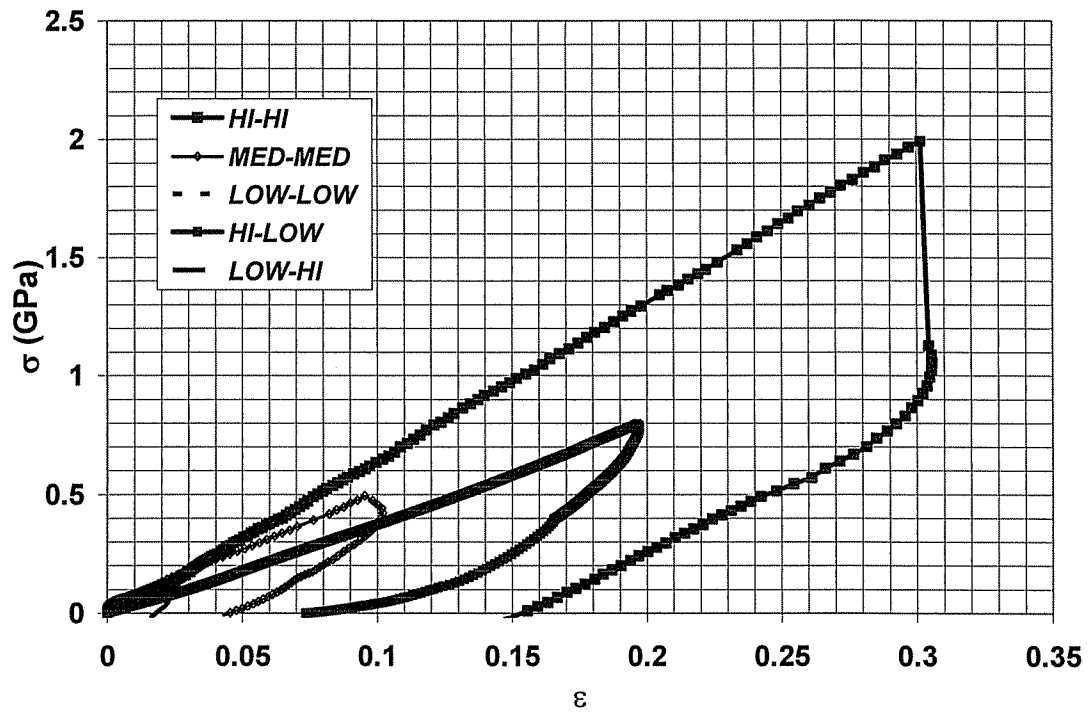


Figure 6

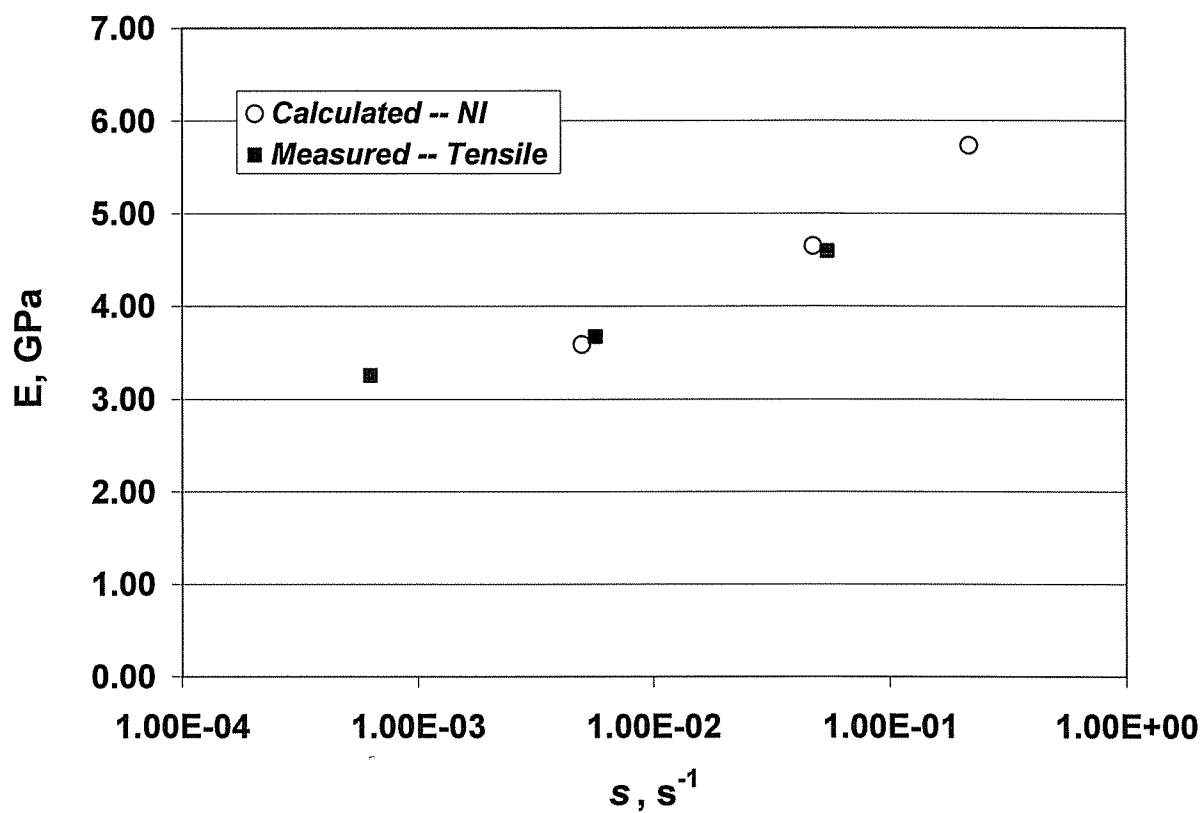


Figure 7

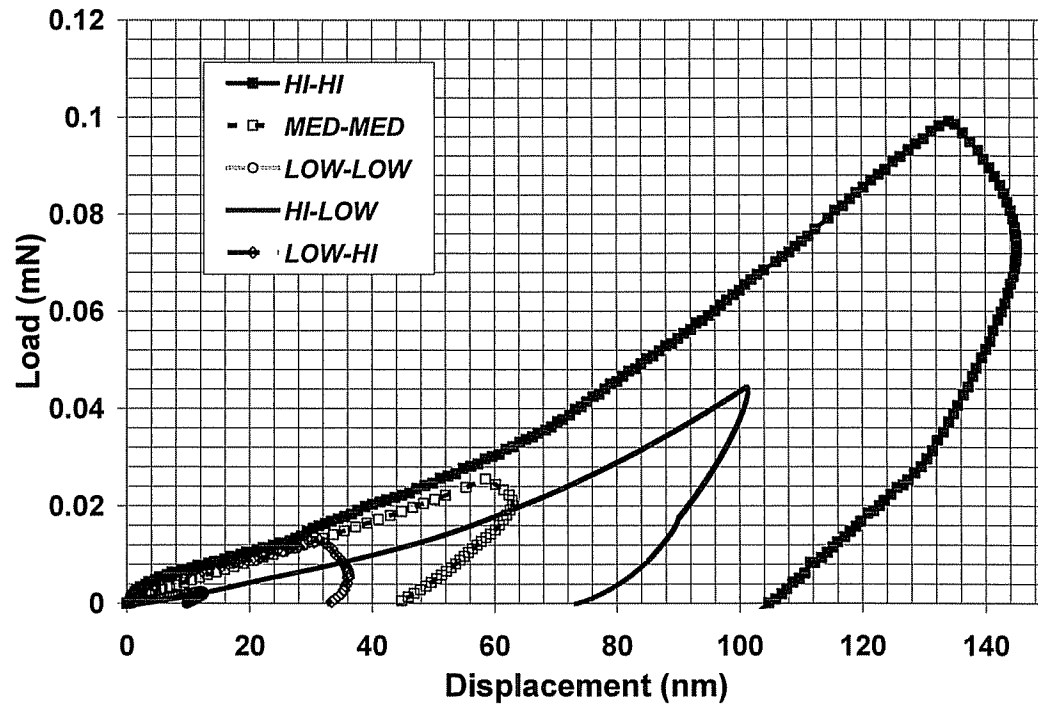


Figure 8

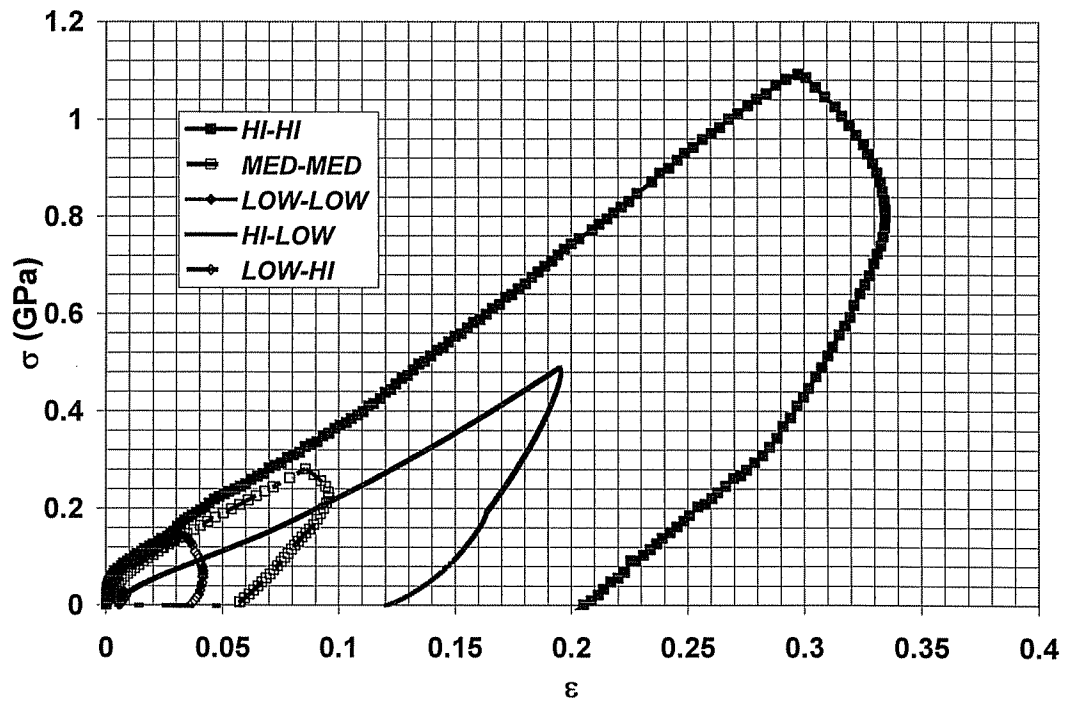


Figure 9

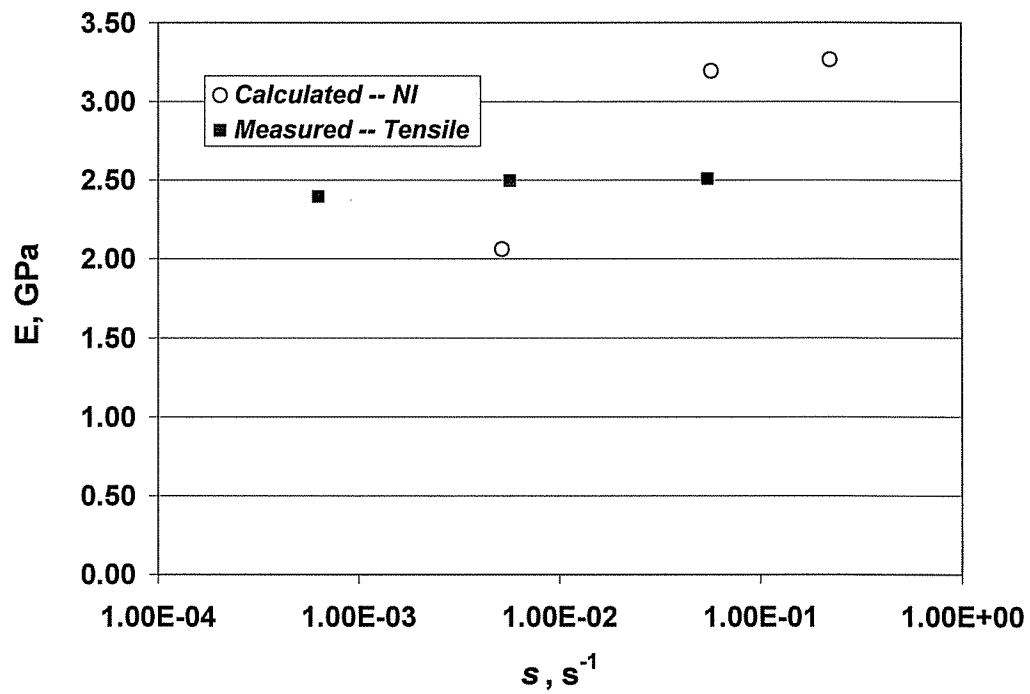


Figure 10

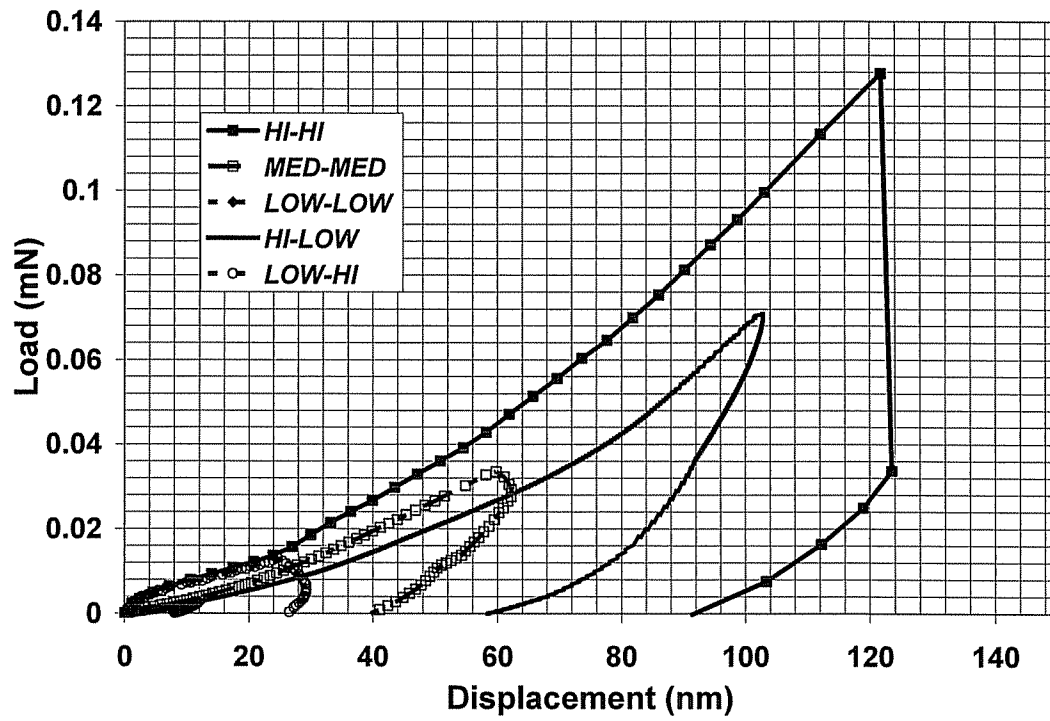


Figure 11

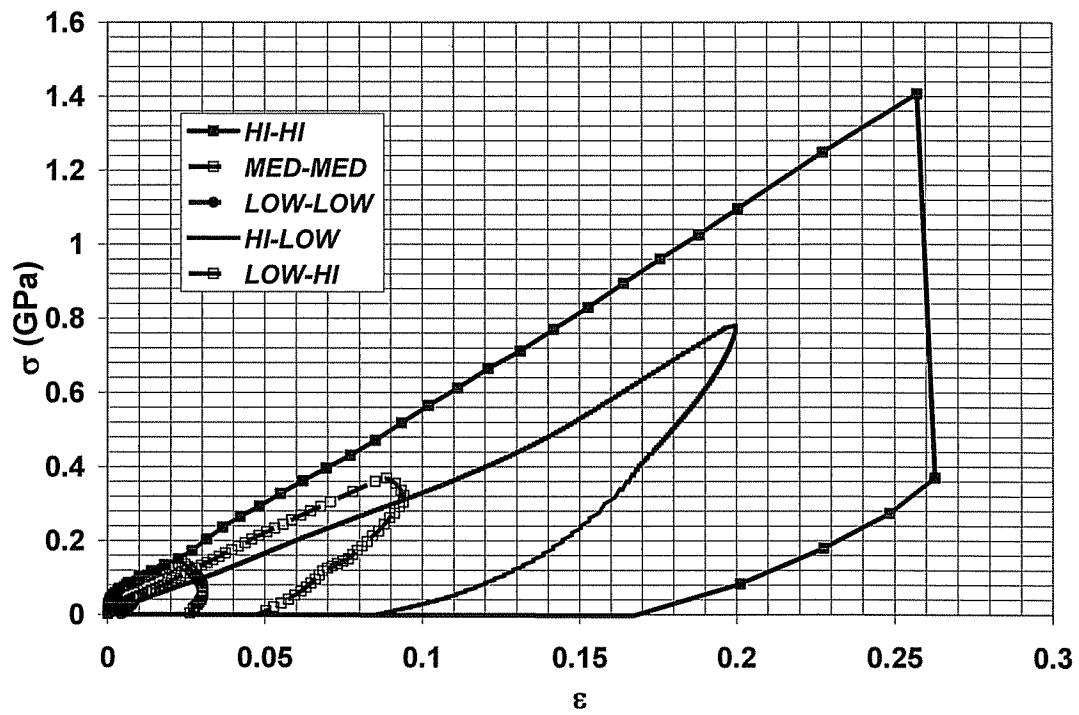


Figure 12

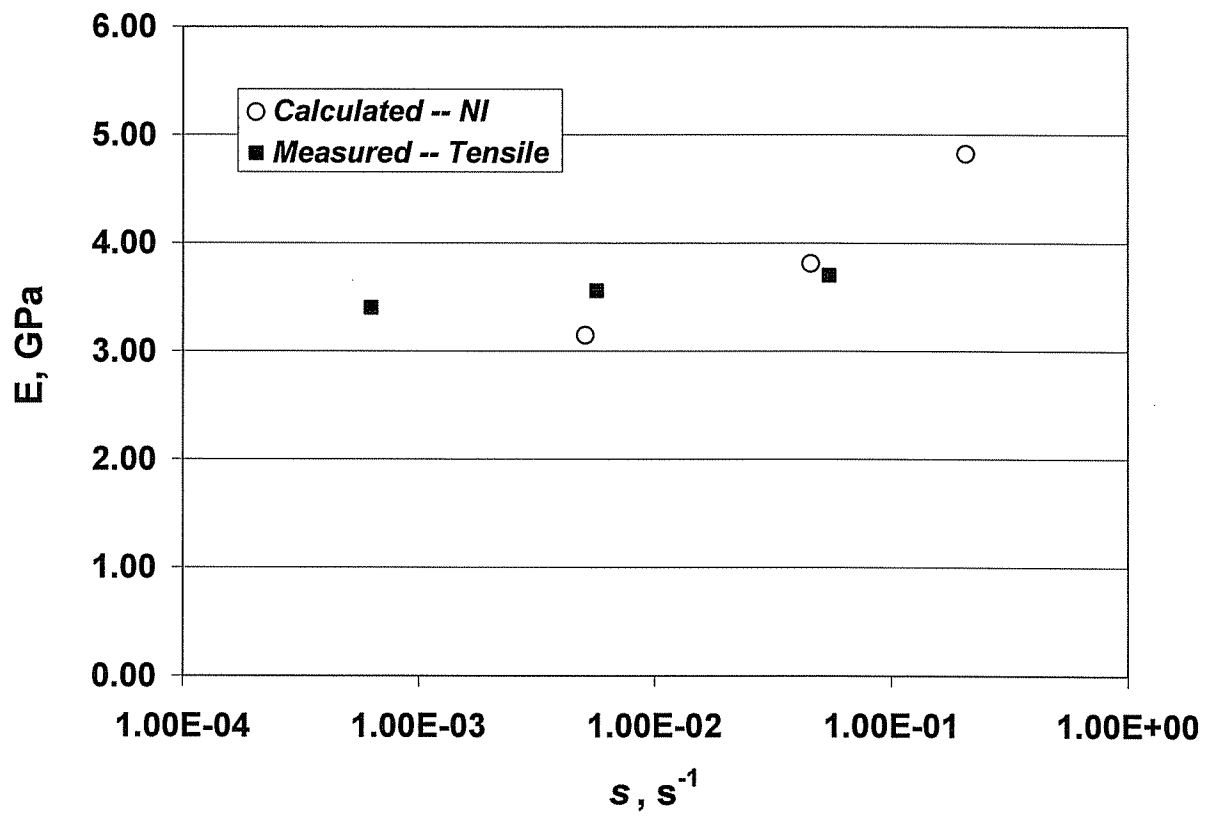
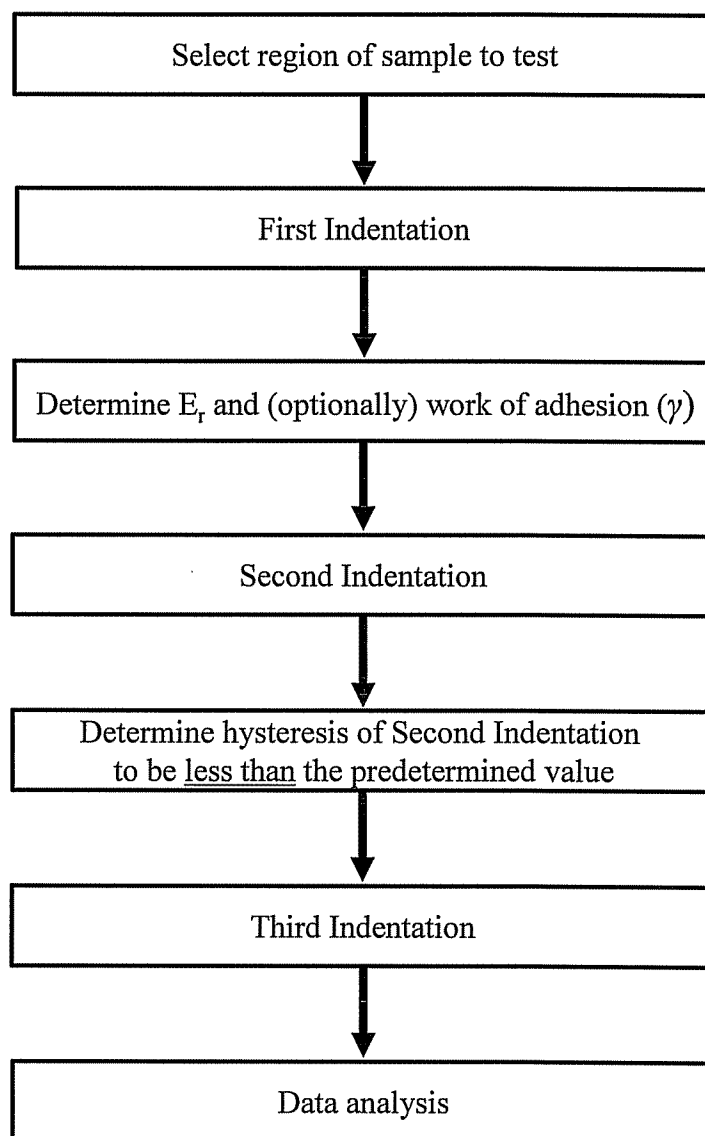
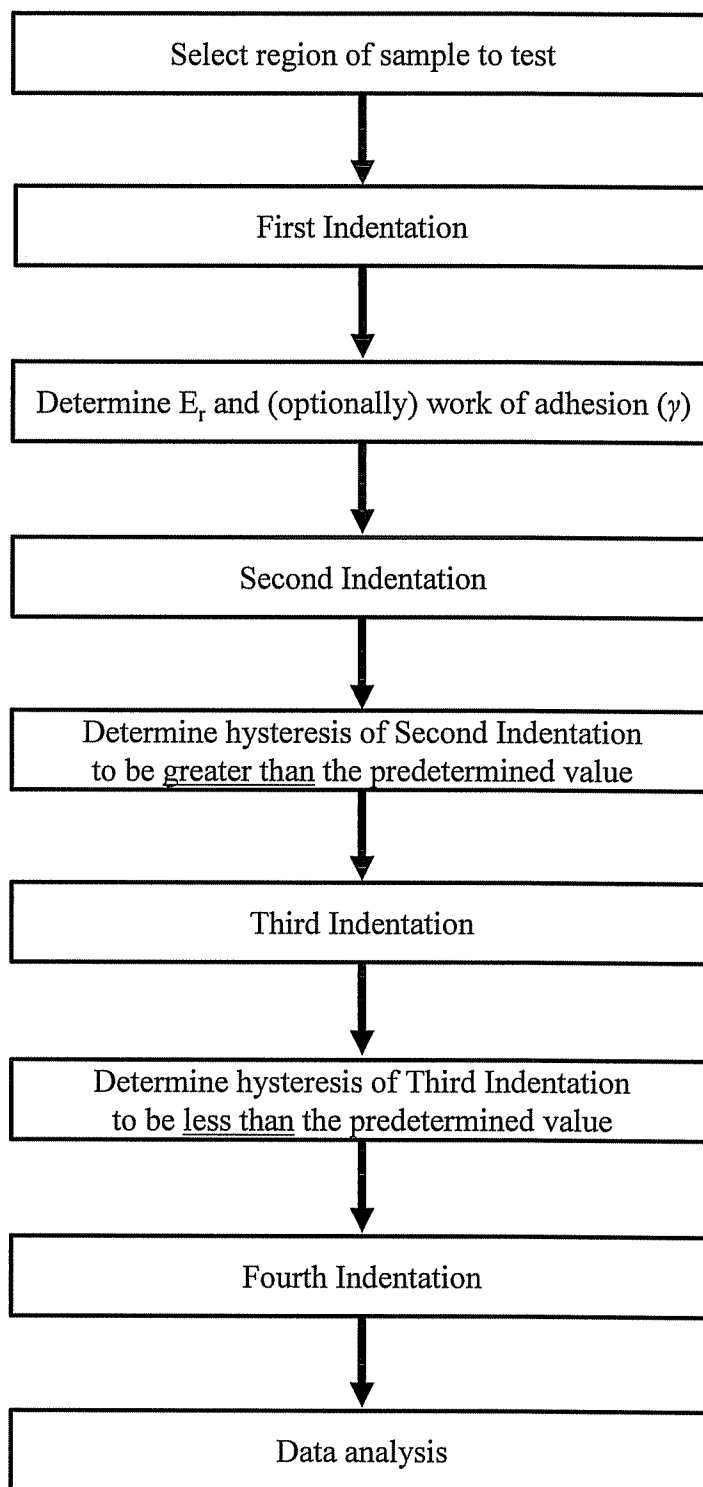
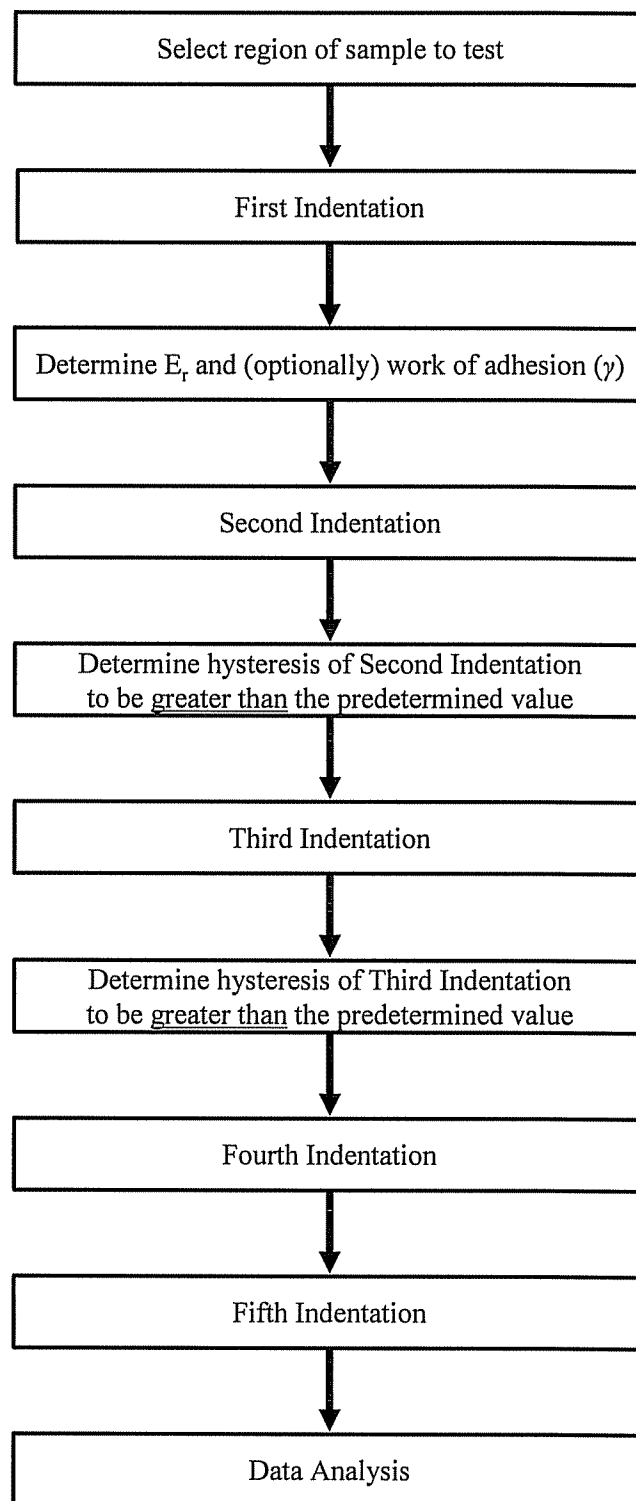


Figure 13

***FIGURE 14***

***FIGURE 15***

***FIGURE 16***