공학석사 학위논문

Evaluation of Elastic Modulus of Polymeric Materials Using Nanoindentation

나노압입시험을 이용한 폴리머 소재의 탄성계수 평가

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서울대학교 대학원
재료공학부
전 혜 련

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이 논문을 공학석사 학위논문으로 제출함

2017년 12월

서울대학교 대학원

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전 혜 련

전혜련의 석사학위논문을 인준함

2017년 12월

위 원 장 유웅열 (인)

부위원장 권 동 일 (인)

위 원 선정윤 (인)

Abstract

Jeon, Hyeryeon
Dept. Materials Science and Engineering
The Graduate School
Seoul National University

The elastic modulus of polymeric materials has significance when its dependence on time, temperature and several environmental conditions is identified. Among them, time-dependency, known as the viscoelasticity, has been widely studied by many researchers. To clarify the time dependency of elastic modulus, evaluation of elastic modulus at various rates is needed. Nanoindentation technique is one of the useful methods to evaluate the viscoelastic properties along with tensile test and dynamic mechanical analysis (DMA). This technique has its advantage in that it is literally able to evaluate the material in small scale. In nanoindentation, the elastic modulus is determined by unloading curve which represents the material's nature to return to its original state. In case of viscoelastic materials, however, the material tends to move toward the loading direction during the unloading process and thus it distorts the shape of load-displacement curve. This is called as "nose" because it has the convex shape in the unloading part of the curve. As a result, the slope of unloading curve, so called stiffness, changes and so does the elastic modulus. This is caused by viscous behavior of the material which is induced by the applied force during the loading process. Therefore, in order to achieve the goal of obtaining the elastic modulus at various rates, this study presents experimental parameters and conditions in which viscous effect on unloading curve can be effectively reduced at the slow unloading rates. In addition, we investigate the criterion which can be used to discriminate whether the viscous effect on the unloading curve is eliminated or not. Based on this criterion, the modulus of elasticity of the polymeric material will be evaluated at various unloading rates under the criterion that the viscous effect disappeared and compared to the results of the conventional experimental condition. Finally, for verification, the comparison with the elastic modulus determined by tensile test will be carried out.

Keyword: Elastic modulus, Nanoindentation, Polymer, Slow rate, Viscoelasticity, Viscous behavior

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Chapter 1

INTRODUCTION

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1.1. Objective and Scope of this Thesis

There has been a growing demand for evaluating viscoelastic materials via nanoindentation. One of the most basic properties that can be obtained from nanoindentation is elastic modulus. This has its significance in viscoelastic materials when it clearly reveals dependence on time, temperature, and previous history of specimen, etc. Especially, time-dependent elastic modulus can be obtained from the unloading curve depending on the unloading rate. However, there is a limitation in evaluating the elastic modulus of viscoelastic materials at various rates, especially slow rates. This is due to an indentation procedure itself and viscous component of viscoelastic materials. Therefore, in order to achieve the goal of obtaining the elastic modulus at various rates, this study presents experimental parameters and conditions in which viscous effect on unloading curve can be effectively reduced at the slow unloading rates. In addition, we investigate the criterion which can be used to discriminate whether the viscous effect on the unloading curve is eliminated or not. Based on this criterion, the modulus of elasticity of the polymeric material will be evaluated at various unloading rates under the criterion that the viscous effect disappeared and compared to the results of the conventional experimental condition. Finally, for verification, the comparison with the elastic modulus determined by tensile test will be carried out

1.2. Outline of the Thesis

The thesis has five chapters. The objective and organization of thesis are introduced in Chapter 1. Chapter 2 gives theoretical background on viscoelastic behavior and also reviews the elasticity of polymeric materials. Chapter 3 presents experimental parameters and conditions in which viscous effect on unloading curve can be effectively reduced at the slow unloading rates. In addition, the criterion which can be used to discriminate whether the viscous effect on the unloading curve is eliminated or not is also presented. In chapter 4, experimental work to verify developed models is described and the results are discussed. Finally, conclusions are given in Chapter 5.

Chapter 2

RESEARCH BACKGROUND

Contents

2.1 Modulus of Elasticity

2.1.1 Definition of Elastic Modulus

Elasticity is the ability of a material to resist to elastic deformation. The deformation is elastic when the material returns to its original shape and dimensions after the applied load is removed. Elastic modulus is a parameter which represents the amount of elasticity. To be specific, it measures the amount of force per unit area needed to obtain a given amount of deformation. The elastic modulus of the bodies in tension and compression is usually represented by the symbol 'E' and is expressed as

$$\mathrm{E} = \frac{\text{normal stress}}{\text{normal strain}} = \frac{\sigma}{\varepsilon} \qquad (2\text{-}1)$$

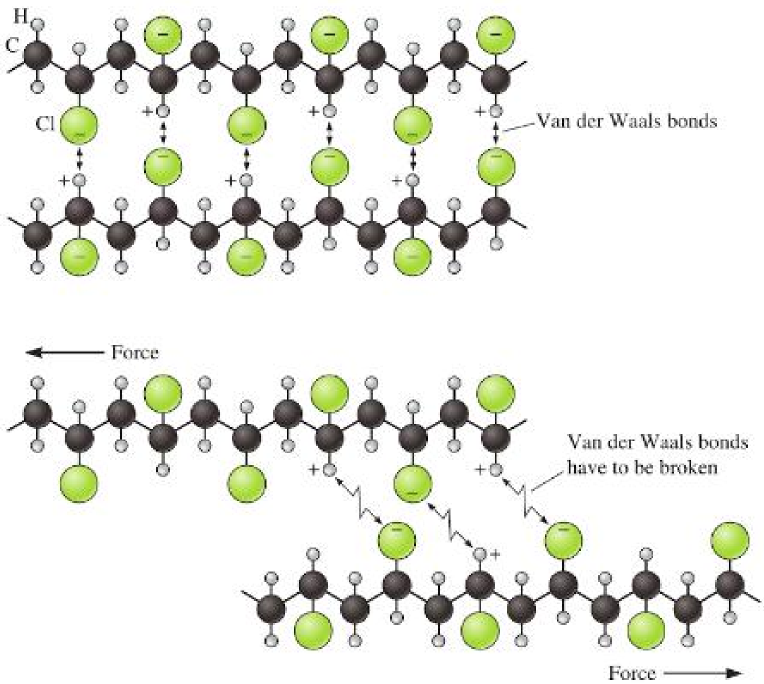
In the SI system, the units of elastic modulus are newton per square metre (N/m^2) or pascal (Pa). As can be seen from the unit of elastic modulus which is equal to stress, the elastic modulus does not depend on the geometry of a body. In other words, it is the physical stiffness of the material itself. [1]

The elasticity of materials is well described by a stress–strain curve. In Hookean's regime, materials exhibit linear elasticity and can be described by a linear relation between the stress and strain which is often supposed to apply up to the elastic limit for most metals or crystalline materials whereas nonlinear elasticity is generally required to model large deformations of rubbery materials even in the elastic range. [2]

2.1.2 Elasticity of Polymers

Elasticity has its origin in the bonds between atoms or molecules. In case of metals, elasticity is the result of bond stretching. The atomic lattice changes size and shape when force is applied. This distortion changes the energy state between atoms as they move apart from their equilibrium distance. When force is removed, the lattice goes back to the original lower energy state. On the other hand, in case of polymers, elasticity is contributed by two thermodynamic factors which are schematically shown in Figure 2.1. [3] One is an internal energy change which is related to the intermolecular interactions such as van der Waals, dipole and hydrogen bonds. This is called energy elasticity. The work required to produce deformation is stored as internal energy in the body and released again when the stress is reduced. The covalent bonds do not contribute significantly to the elastic properties. [4, 5] The other is an entropy change which is a result of untangling and entangling of the molecular chains on the application of force. When the chains are stretched by applied force, their alignment increases the entropy. When forces are removed, the molecular chains go back to the original high entropy state. This is called entropy elasticity. To sum up, elasticity of polymer is induced by two factors: energy elasticity and entropy elasticity.

The difference between two elasticities is as follow. The energy elasticity has an instantaneous nature, whereas entropy elasticity is sensitive to rates because it is related to local molecular mobility. [6] Thus, the entropy elasticity explains a time-dependent behavior of polymers from a thermodynamic standpoint.



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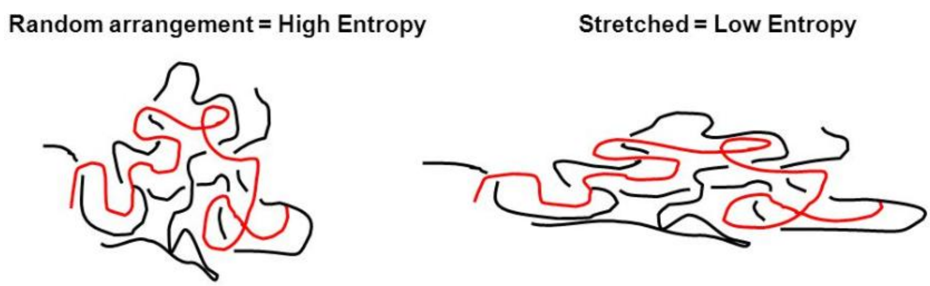


(b)

Figure 2.1. Two thermodynamic factors of polymer elasticity: (a) energy elasticity [3] (b) entropy elasticity

2.1.3 Measurement Methods for Elastic Modulus of Polymers

2.1.3.1 Tensile Test

Tensile test is a method for determining the tensile properties of materials in the form of a standard dumbbell-shaped test specimen. This sample is placed in the grips of the testing machine and slowly extended until it fractures. During this process, an extension indicator(extensometer) records the distance between two designated points within the gauge length of the sample against the applied force. The data is manipulated in the form of stress and strain. Strain, ε, is calculated using the following equation:

$$\varepsilon = \frac{\Delta \mathrm{l}}{l_0} = \frac{l - l_0}{l_0} \qquad (2\text{-}2)$$

where $\Delta \mathrm{l}$ is the change in gauge length, l_0 is the initial gauge length, and l is the final gauge length. Stress, σ, is calculated using the following equation:

$$\sigma = \frac{\mathrm{F}}{\mathrm{A}} \qquad (2\text{-}3)$$

where F is the tensile force and A is the nominal cross-section of the specimen. The data points can be graphed into a stress–strain curve as shown in Figure 2.2 (a). [7]

For measuring the tensile properties of polymers, ASTM standard [8] specifies several test conditions and adequate analysis methods. Among tensile properties, elastic modulus is determined from the slope of the linear portion of the stress-strain curve which is calculated by dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain as indicated in Eq. (2-1). Because the exact stress-strain characteristics of polymer are highly dependent on rate of application of stress, elastic modulus of polymers are recommended to evaluate at various testing speeds.

2.1.3.2 Dynamic Mechanical Analysis (DMA)

DMA is a technique used to measure the mechanical and viscoelastic properties of materials. In DMA, the sample is subjected to a periodic stress which is the result of one of several different modes of deformation (bending, tension, shear and compression) as shown in Figure 2.2 (b) and material’s responses to that stress are analyzed. From this, viscosity and elasticity (stiffness) can be obtained from the phase lag and sample recovery. Modulus are measured as a function of time or temperature. There are three kinds of modulus in DMA test:

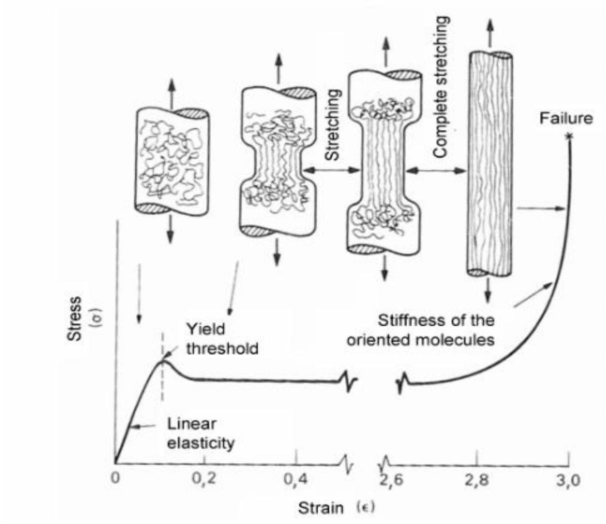
$$\mathrm{E}' = \frac{\sigma_0}{\varepsilon_0} cos\delta \ (storage\ modulus)$$

$$\mathrm{E}'' = \frac{\sigma_0}{\varepsilon_0} sin\delta \ (loss\ modulus) \tag{2-4}$$

$$|E^*| = \sqrt{(\mathrm{E}')^2 + (\mathrm{E}'')^2}^2 \ (complex\ modulus)$$

The storage modulus measures the stored energy, representing the ability to recover from deformation (elastic portion), and the loss modulus measure the ability to lose energy as heat (viscous portion). The complex modulus is composed of the storage modulus and the loss modulus. [9]

These two methods are useful and widely used. However, they have limitations on a small scale because the specific shape and size are needed. Therefore, more suitable test method is needed to obtain the elastic modulus of polymers at a small scale. The nanoindentation technique being introduced in the next section is the one.



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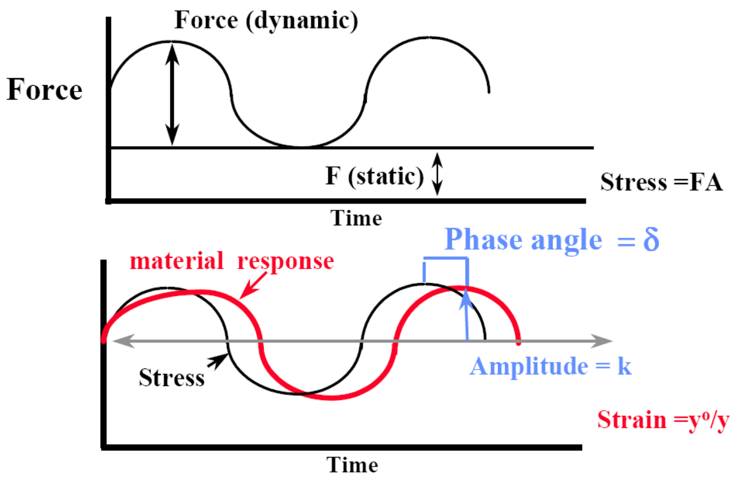


(b)

Figure 2.2. Measurement methods for elastic modulus of polymers:

(a) tensile test [6] (b) DMA

2.2 Nanoindentation Technique

2.2.1 Introduction

Indentation test is a mechanical test putting an indenter on the surface of a sample. This test has its origin in the conventional hardness test such as Vickers and Brinell hardness testing etc. The conventional hardness test only measures the hardness from residual imprint size, which implies that it indicates only plastic behavior of the material. However, it has been enormously improved by introducing instrumented indentation technique (IIT). According to ASTM E2546 [10], instrumented indentation technique is "a mechanical test that measures the response of a material to the imposed stress and strain of a shaped indenter by forcing the indenter into a material and monitoring the force on, and displacement of, the indenter as a function of time during the full loading-unloading test cycle." In case of instrumented indentation test, the estimation of the contact area and elastic property from the unloading curve is possible because whole test cycle is recorded resulting in load-displacement curve. Therefore, the elastic modulus as well as the hardness of the test materials can be measured by using IIT. [11-14]

Nanoindentation is a kind of an indentation test in which the penetration depth is measured in nanometer scale rather than microns or millimeter scale. [15] This was supported by technological developments such as reduction of the size of tips manufactured and improvement of the accuracy and resolution of depth and load measurement of the indentation test. Its popularity is primarily due to the increased interest in thin films and specimens with small volumes as motivated by modern applications.

2.2.2 Determination of Elastic Modulus by Nanoindentation

As it become possible to measure the unloading portion of indentation curve indicating the elastic property of a material, studies were carried out to measure the elastic modulus through the load and displacement sensing indentation testing. The following is the conventional procedure for extracting elastic modulus from the load and displacement curve. The whole process is based on elastic contact mechanics. Hertz [16] originally developed the contact problem between two elastic bodies and it was subsequently studied by Boussinesq [17] using the methods of potential theory. Sneddon [18] derived the load–displacement relationship for an arbitrary shaped indenter by using the approach taken by Boussinesq. The Sneddon's solution is as follow:

$$P = \frac{2\mathrm{E}\tan\alpha}{\pi(1-\upsilon^2)}h^2 \qquad (2\text{-}5)$$

where P is the load measured by the indenter, E and ν are the Young's modulus and Poisson's ratio of the material that is being indented, α is the half angle of the indenter, and h is the displacement of the indenter. This is based on the assumption of a linearly elastic half-space and rigid conical indenter. Therefore, Sneddon's solution is only valid for linearly elastic.

In the flat punch approximation used by Doerner and Nix [11], the contact area remains constant as the indenter is withdrawn, and the resulting unloading curve is linear. However, experiments have shown that unloading curves are distinctly curved. By assuming that the initial unloading segment of the load–displacement curve is linearly elastic, the slope of the load–displacement curve is given by differentiating Eq. (2-5) with respect to h.

$$\frac{dP}{dh} = \frac{4\mathrm{E}\tan\alpha}{\pi(1-\upsilon^2)}h \qquad (2\text{-}6)$$

By following the process of algebraic manipulation, [15]

$$\frac{dP}{dh} = \frac{2\sqrt{A}E}{\sqrt{\pi}(1-\upsilon^2)} \quad (2\text{-}7)$$

where A is the projected area of contact of the indenter. For a Berkovich/Vickers indenters, the angle α = 70.3°, and the corresponding projected area, A is given by

$$A = \pi tan^2\alpha {h_c}^2 = 24.5{h_c}^2 \quad (2\text{-}8)$$

where h_c represents the contact depth and is given by [15]

$$h_c = h_{\max} - \varepsilon \frac{P}{dP/dh} \quad (2\text{-}9)$$

where ε is a constant that depends on the geometry of the indenter. (ε=0.72 for a conical punch, ε=0.75 for a parabolic of revolution, and ε=1 for a flat punch)

Thus, measurement of the elastic modulus follows from its relationship to contact area and the measured unloading slope through the relation:

$$\frac{E}{(1-\upsilon^2)} = \frac{1}{2\beta}\sqrt{\frac{\pi}{A}}\frac{dP}{dh} \tag{2-10}$$

where β is a non-dimensional correction factor to account for deviations from the original stiffness equation. (β = 1.012 for Vickers indenter, and β = 1.034 for Berkovich indenter) [19] The effect of non-rigid indenters, which is against the assumption of Sneddon's solution, can be accounted for by defining a reduced modulus, Er. [12]

$$\frac{1}{E_r} = \frac{(1-\upsilon^2)}{E} - \frac{(1-\upsilon_i^2)}{E_i} \tag{2-11}$$

where E and ν are Young's modulus and Poisson's ratio for the specimen and E_i and v_i are the same parameters for the indenter. Therefore, the equation is transformed as follow:

$$S = \frac{dP}{dh} = \beta\frac{2}{\sqrt{\pi}}E_r\sqrt{A} \tag{2-12}$$

where S=dP/dh is the experimentally measured stiffness of the upper portion of the unloading data approximated by the power law relation. The load-displacement curve and parameters which are obtained from it are shown schematically in Figure 2.3

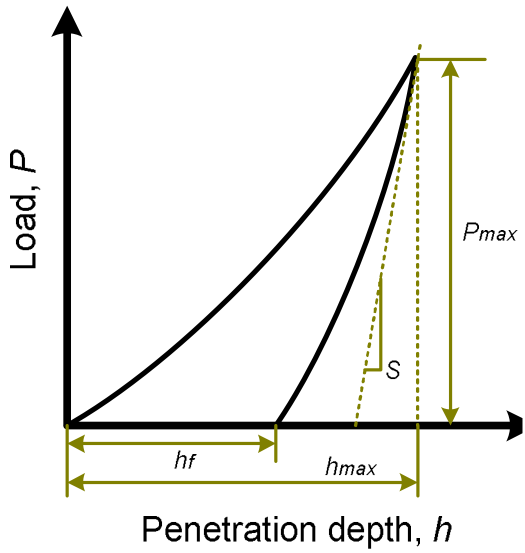


Figure 2.3. Schematic representation of load-displacement curve and parameters which are obtained from the curve

2.3 Viscous Effect of Polymeric Materials

2.3.1 Viscoelasticity

Polymer materials are composed of great length of molecular chains which are intertwined each other. Due to their unique molecular structure compared to other materials such as metals and ceramics, it causes a different response to mechanical load. Specifically, these materials behave in some instances as elastic solids and in some instances as viscous fluids; that is, being viscoelastic.

2.3.2 Viscous Effect

Viscoelasticity results in time-dependent mechanical behavior. One of the major phenomena is the retarded deformation with respect to instantaneous application and release of stresses. [20] In order to identify this, one needs to know the deformation of viscous liquid and elastic solid as a function of time. In case of elastic solid, deformation instantly increases at some definite level and then stays constant. On the other hand, the deformation of viscous liquid increases linearly depending on time.

This is schematically shown in Figure 2.4(a). As a result, the intermediate materials which show both viscous flow and elastic behavior represent the slow development of deformation as shown in Figure 2.4(b). For better understanding of this delayed deformation, let's look at the four-parameter model which is one of the viscoelastic models. The schematics of this model is illustrated in Figure 2.5. This model provides a qualitative representation of time-dependent behavior of the viscoelastic materials. Retarded deformation can be divided in two parts; one is recoverable retarded elastic deformation and the other is irrecoverable viscous flow. The former is related to the parallel connected spring and dashpot components and the latter is associated with the dashpot component which is serial connected in the model. [21] From a molecular standpoint, retarded elastic deformation is the result of the resistance of polymer chains with respect to coiling and uncoiling attributed by transformation of a given equilibrium conformation into a biased conformation with oriented structure depending on the direction of applied force. The process of coiling and uncoiling only occurs in retarded manner. The viscous flow followed on the retarded elastic deformation is the result of the slippage of polymer chains. [21] Overall, retarded deformation is a result of viscous effect.

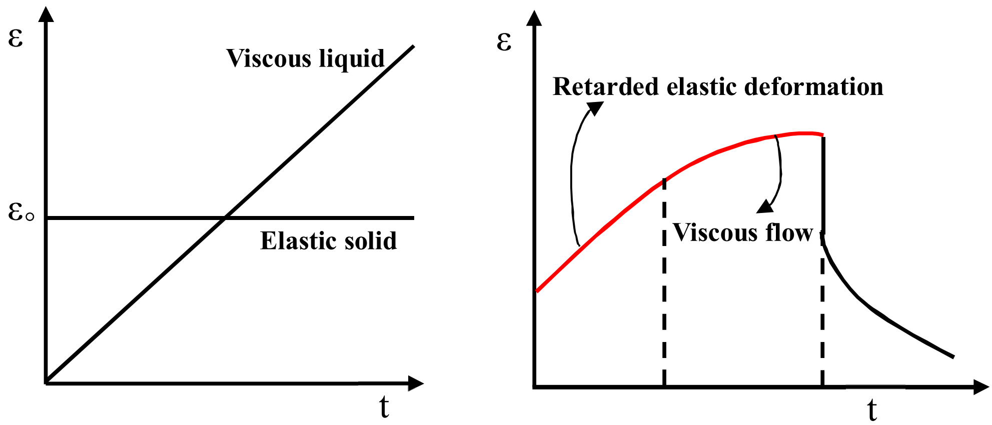


Figure 2.4. Deformation of (a) an elastic solid and a viscous liquid and (b) a viscoelastic material under constant stress

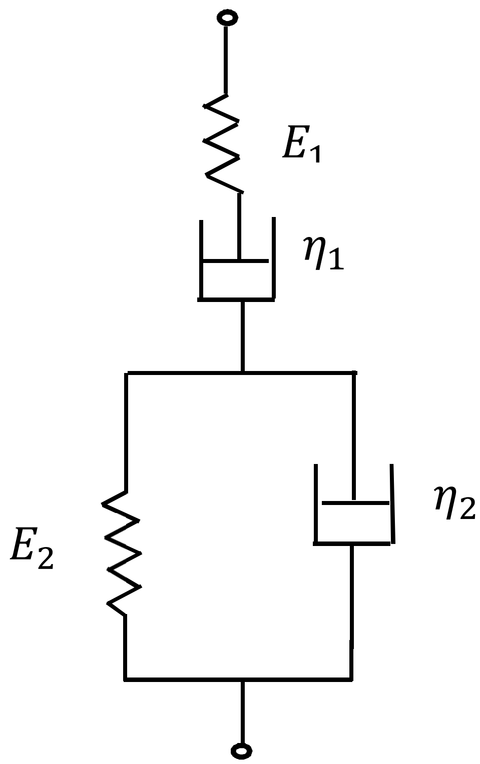


Figure 2.5. Schematic of the four-parameter model

2.3.3 Relationship between Elastic Modulus and Viscosity

Elastic modulus is originally a parameter which represents the amount of elasticity. However, elastic modulus of polymer does not represent the pure elastic property of polymer. As mentioned previous section, polymer is a viscoelastic material which exhibits both viscous and elastic characteristics when undergoing deformation. This implies that total deformation includes both viscous and elastic components. Therefore, in case of viscoelastic materials, elastic modulus reflects the influence of the two components. This can be easily understood by the standard linear solid model as shown in Figure 2.6. This model describes the behavior of a viscoelastic material using combination of the Maxwell model and a Hookean spring in parallel. Following is a physical relation of this model in the Laplace plane [6]:

$$\bar{\sigma} = \mathcal{E}\bar{\epsilon} \tag{2-13}$$

where for this model the parameter $\mathcal{E}$ is

$$\mathcal{E} = E_1 + \frac{E_2 s}{s + \frac{\eta}{E_2}} \tag{2-14}$$

Eq. (2-3) recalls the Hooke's Law $\sigma = E\epsilon$ but in the Laplace plane and is called the associated viscoelastic constitutive equation. As can be seen from the equation, the parameter $\mathcal{E}$ contains both elastic and viscous components.

Then, let's look at the effect of the viscous component on the modulus of elasticity. Purely elastic materials do not dissipate energy when a load is applied, then removed. However, a viscoelastic substance loses energy when a load is applied, then removed. [22] This is due to the viscous nature of the material. Viscosity is the result of internal friction caused by the intermolecular interactions between molecules that resists its flow. Therefore, these molecular actions cause the energy loss during deformation. This can be estimated through hysteresis experiment. In hysteresis experiment, a material is loaded and unloaded, producing stress-strain curve. For a linear elastic material, the loading and unloading curves overlap as shown in Figure 2.7(a). On the contrary, for the viscoelastic materials, the loading portion of the stress strain curve is higher than unloading curve as shown in Figure 2.7(b). The area between the loading and unloading curves represents the dissipated energy and the bottom area of the unloading curve shows the recovered energy. The ratio of the recovered and dissipated energy depends on the applied strain and strain rate. In general, viscoelastic materials behaves in a more viscous manner at lower strain rates than at high strain rates. This implies that relatively larger deformation energy is dissipated as heat by viscous flow at lower strain rate. [23] This is the reason why viscosity of a viscoelastic substance gives the substance a strain rate dependence on time. Therefore, it is expected that elastic modulus increases as the strain rate increases because the time for adjusting and absorbing the applied load by viscous motions of the material become shorter.

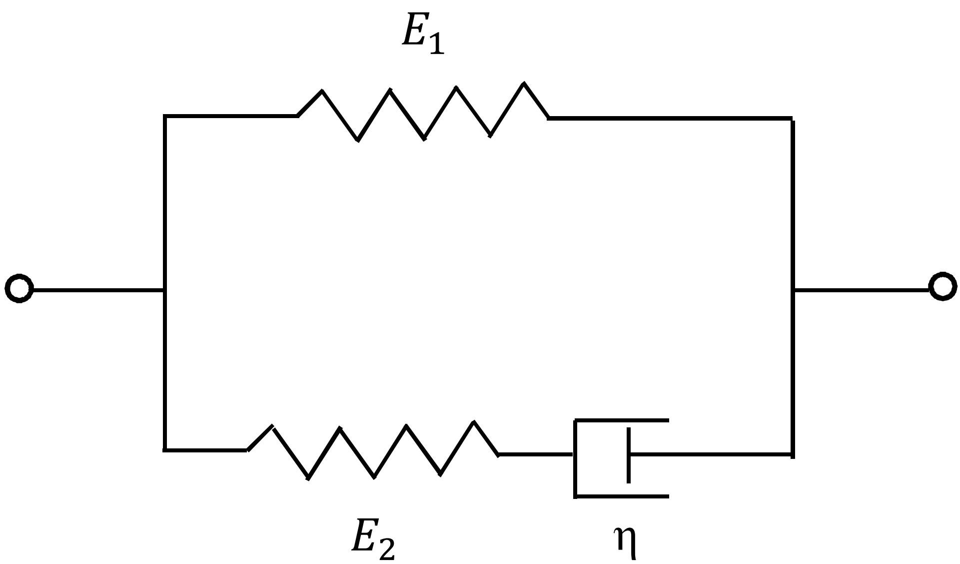
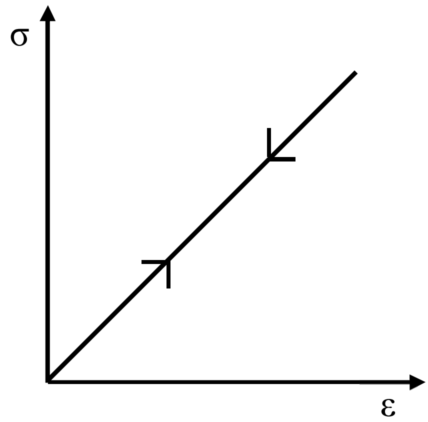


Figure 2.6. Schematic of standard linear solid model



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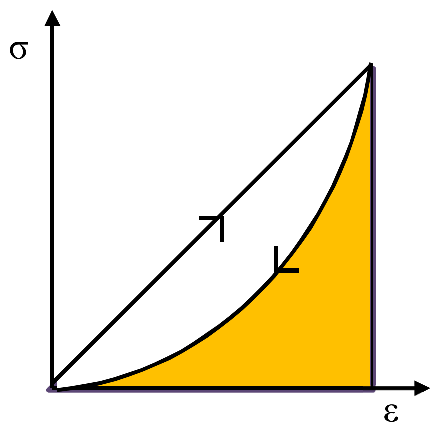


Figure 2.7. Stress-strain curve of (a) a linear elastic material, (b) a viscoelastic material in hysteresis experiment

Chapter 3

Criterion for the Viscous Effect on Unloading Curve

Contents

3.1 Motivation and Research Flow

There has been a growing demand for evaluating viscoelastic materials via nanoindentation. One of the most basic properties that can be obtained from nanoindentation is elastic modulus. This has its significance in viscoelastic materials when it clearly reveals dependence on time, temperature, and previous history of specimen, etc. [8] Especially, time-dependent elastic modulus can be obtained from the unloading curve depending on the unloading rate.

However, there is a limitation in evaluating the elastic modulus of viscoelastic materials at various rates, especially slow rates. This is due to an indentation procedure itself and viscous component of viscoelastic materials. To understand this, it is essential to know the assumption of the elastic modulus first in indentation test. The indentation procedure consists of loading and unloading processes; the former indicates the complex behavior of plasticity and elasticity of the material and the latter represents the elastic behavior of the material. The relationship between unloading process and the elasticity can be explained by the recovery phenomena of the material which reflects the material's nature to return to its original state. This assumes that the material is oriented in the direction of recovery.

Based on this, the elastic modulus can be obtained from the unloading part of load and displacement curve. However, in the case of viscoelastic materials, a phenomenon that is against the assumption is observed. In other words, the viscoelastic materials tend to move toward the loading direction during the unloading process as shown in Figure 3.1. This inevitably occurs in the indentation procedure because the loading process is preceded prior to the unloading process. In the loading process, a viscous behavior towards the loading direction is induced. Therefore, it is necessary to evaluate the elastic modulus considering the viscous effect on the unloading process.

Following is an outline of the research. "Nose phenomenon" which is the result of viscous effect on unloading process will be introduced and previous research that has been conducted to address this issue and their limitations will be discussed. An effective experimental method for slow unloading rates will be suggested and a criterion for the viscous effect on unloading curve will be clarified through the deductive method.

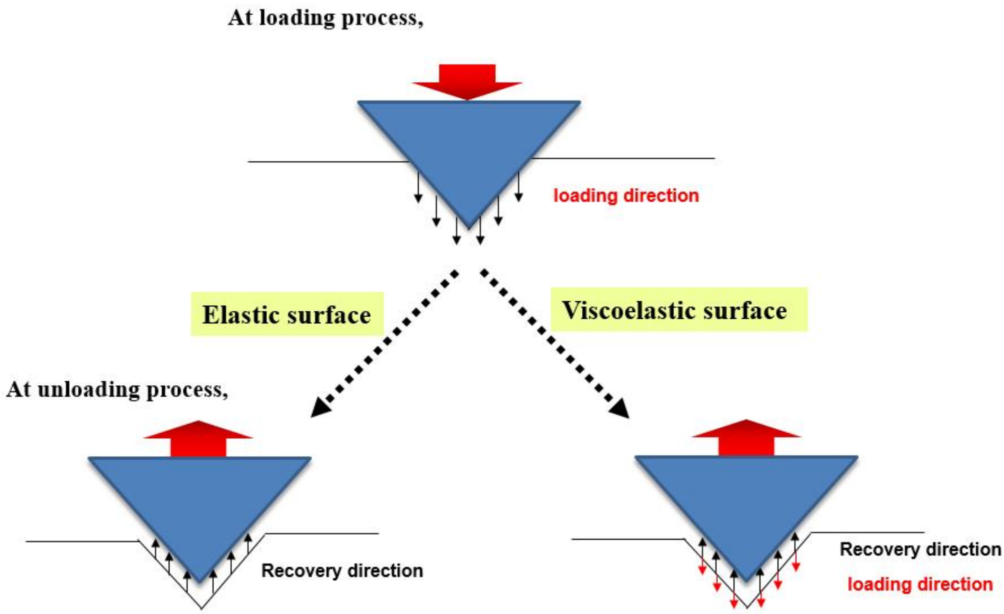


Figure 3.1. Difference between elastic and viscoelastic surface during the indentation process.

3.2 Viscous Effect on Unloading Process

3.2.1 Nose Phenomenon at Unloading Curve

“Nose phenomenon” has been reported by many researchers who study the viscoelastic materials using nanoindentation.[24-28] This literally refers to the appearance of a convex shape which looks like nose on the unloading curve as illustrated in Figure 3.2. [24] This occurs when the displacement increases whereas the load decreases. Figure 3.3 [29] illustrating the force and contact area over time also shows this ironical phenomenon as well. As mentioned in previous section, this is caused by the viscous behavior towards the loading direction is induced in the loading process. In other words, time-dependent behavior of materials, retarded deformation, is derived from loading process. Due to the applied force during the loading process, this time-dependent behavior continues even after the unloading process starts. Finally, the shape of the unloading curve is changed and the slope of unloading curve, so called stiffness, which is an important for determining the elastic modulus is increased.

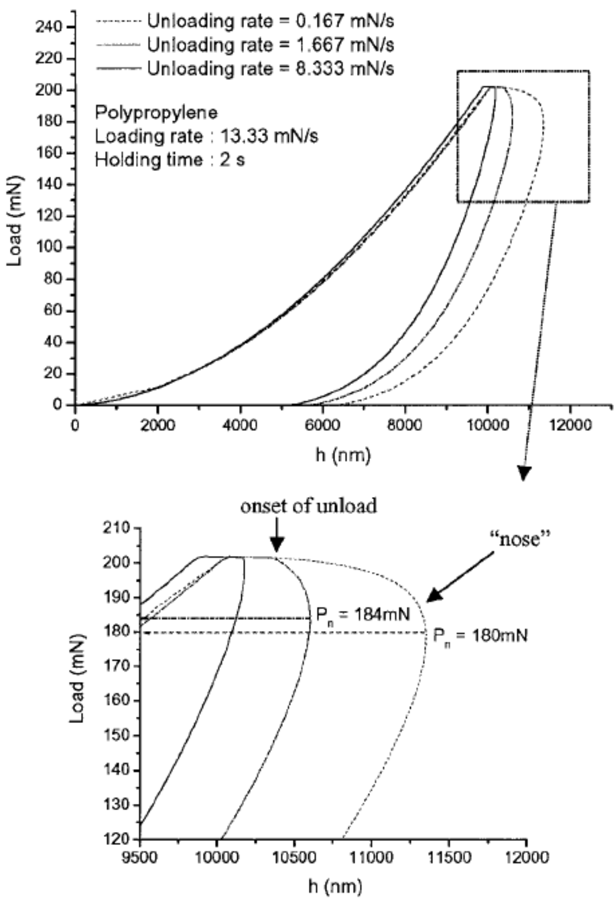


Figure 3.2. **"**Nose phenomenon" occurring at unloading curve [24]

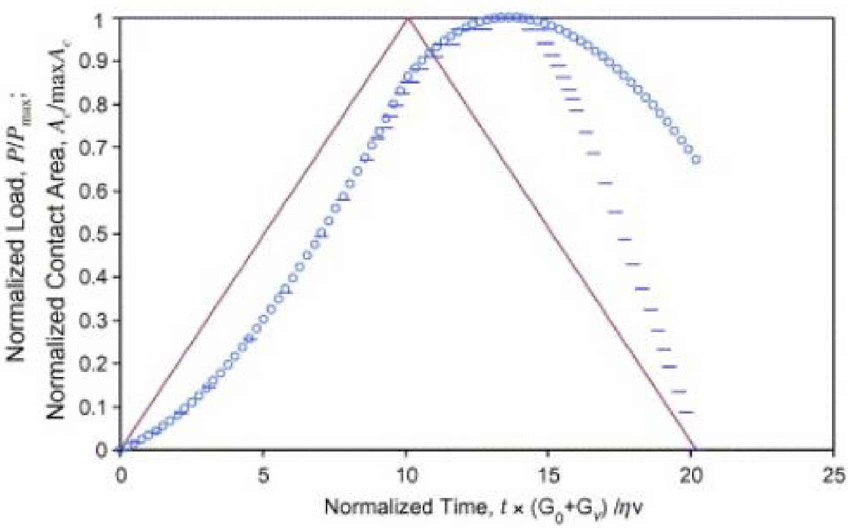


Figure 3.3. Disharmony of the force and contact area over time[29]

3.2.2 Limitation of Previous Research

In order to minimize or remove the viscous effect from the unloading curve, several methodologies have been suggested. One is an analytical method which is proposed by Oliver-Pharr.[12] According to their research, the slope of unloading curves, stiffness, obtained from the first unloading and last unloading process which is done including peak load hold periods in the loading sequence are very different. They found that the reason for this is a significant amount of time dependent plastic effects during the first unloading and those cause the slope of the upper portion of the unloading curve to be abnormally high. Therefore, they proposed the power law fitting method which produces a stiffness at first unloading is only slightly greater than that derived from the last unloading curve as shown in Figure 3.4.[12] This means that this method is less sensitive to viscous deformation than the experimental method which is introduced by the peak load hold periods. For this reason, the power law method is not enough to minimize the viscous effect for the materials which have relatively high viscosity like polymers.

Another method is an experimental method. Two representative methods are as follows: 1) fast unloading rate[24,29,30] and 2) long holding time at peak load.[12,31] Both schematics are given by Figure 3.5. [30, 31] Fast unloading rate is inadequate to evaluate the elastic modulus at diverse unloading rate, especially slow rate because the unloading rate is fixed at a high one. In case of the method of hold time at peak load, the slower the unloading rate, the longer the hold time is required. Therefore, this method is limited to be solely used at very slow rate. It seems that it should be used with another method of lowering the viscous effect at slow unloading rates. Above all, there is no specific criterion for viscous effect on unloading curve. Therefore, following is the process of determining an effective experimental method for slow unloading rate and the criterion for the viscous effect on the unloading curve through the deductive method.

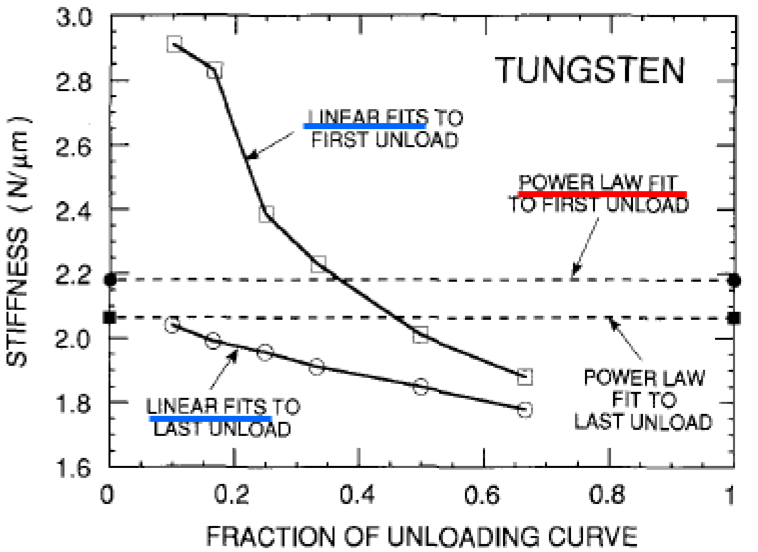
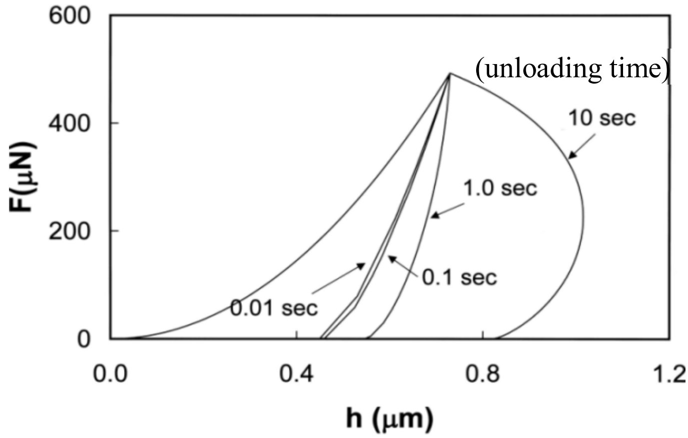


Figure 3.4. Effect of power law fitting method [12]



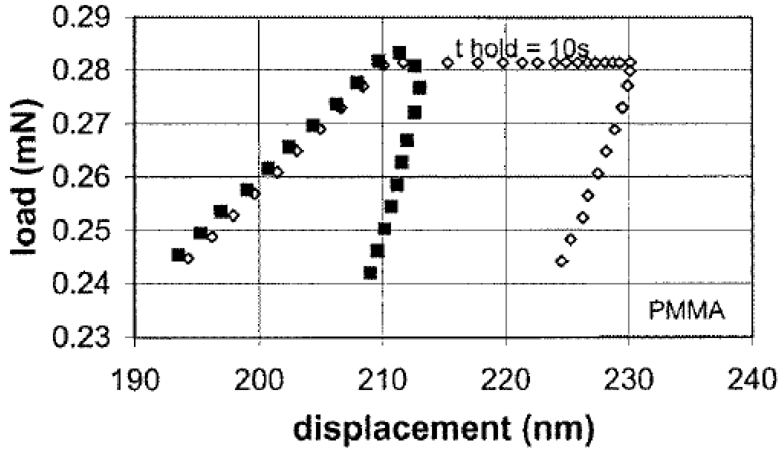


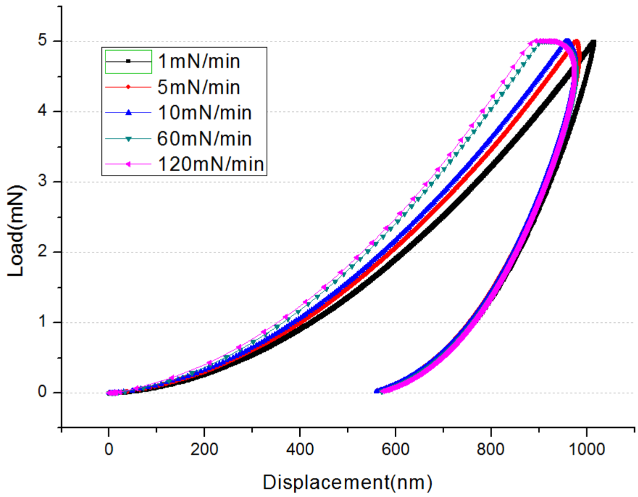
Figure 3.5. Tow representative methods for diminishing viscous effect:

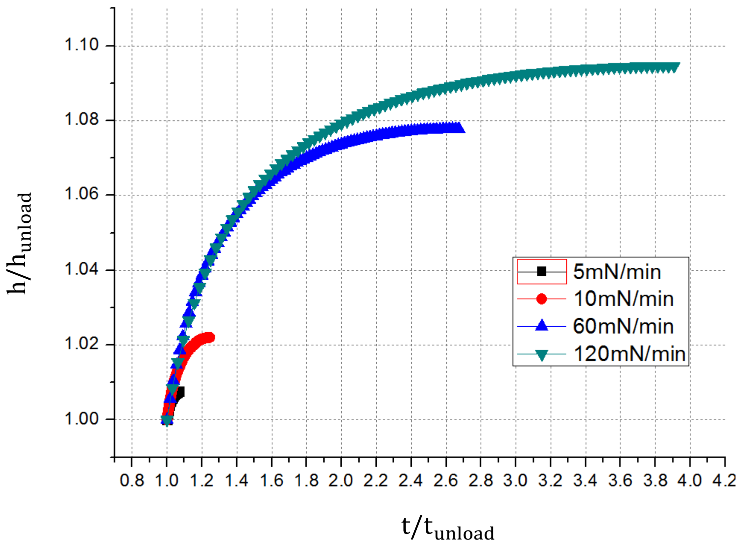
(a) Fast unloading rate[30] (b) long holding time at peak load [31]

3.3 Determination of Criterion for the Viscous Effect on the Unloading Curve

3.3.1 Experimental Method for Slow Unloading Rates

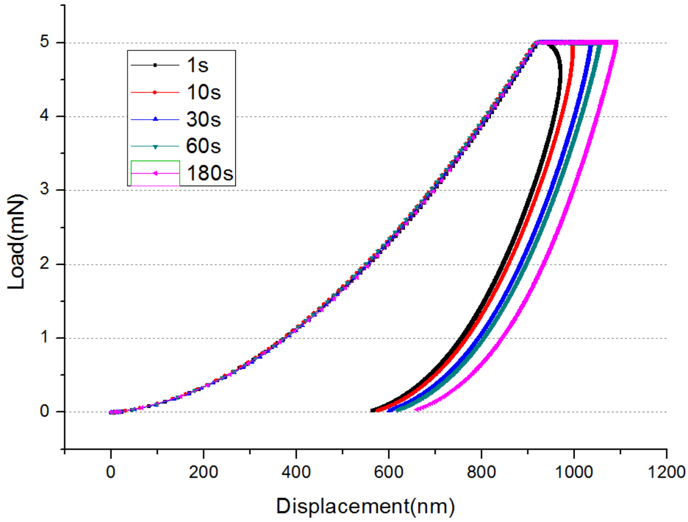
As mentioned in 3.1, elastic modulus has its significance in viscoelastic materials when it clearly reveals dependence on time. In order to satisfy this, the elastic modulus is required to evaluate at various rates. However, with slower unloading rates, the shape of unloading curve is further distorted by the viscous effect. This implies that the elastic modulus obtained at slow unloading rate is not valid. Therefore, an experimental method for slow unloading rates is needed to be clarified. To know this, experiments are performed through three experimental conditions which are a loading rate, a hold time at peak load and an unloading rate. The results are illustrated in Figure 3.6, 3.7, and 3.8. As the loading rate decreases and the unloading rate and holding time increases, the increment of the displacement after unloading start ("nose phenomenon" which is the indicator of viscous effect) is reduced and even removed. However, as mentioned before, fast unloading rate is inadequate to evaluate the elastic modulus at diverse unloading rate, especially slow rate because the unloading rate is fixed at a high one. Therefore, the combination of low loading rate and hold time will be the most suitable test condition for slow unloading rates. As can be seen in Figure 3.9, no “nose phenomenon” is observed in all test conditions with a slow loading rate and various holding time combinations. However, no one can be certain that the viscous effect on the unloading curve is eliminated when the "nose phenomenon" is not observed in the unloading curve. Following is the process of determining the criterion for the viscous effect on the unloading curve through the deductive method.

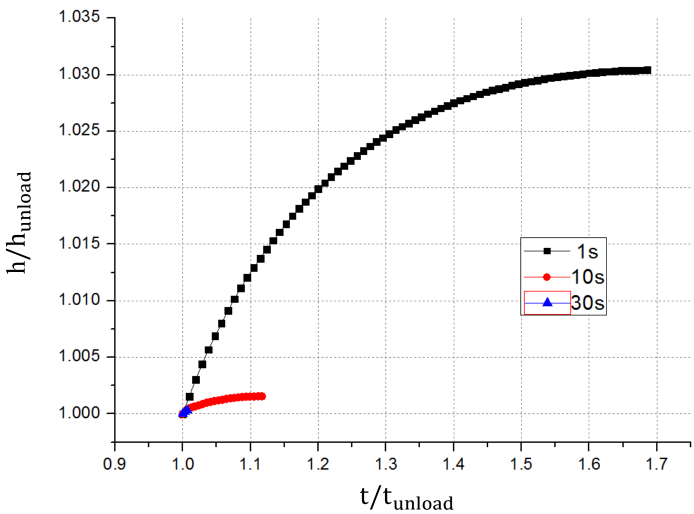




- Material: PMMA
- Maximum load: 5mN
- Loading rate: 1, 5, 10, 60, 120mN/min
- Hold time: 1s
- Unloading rate:3mN/min

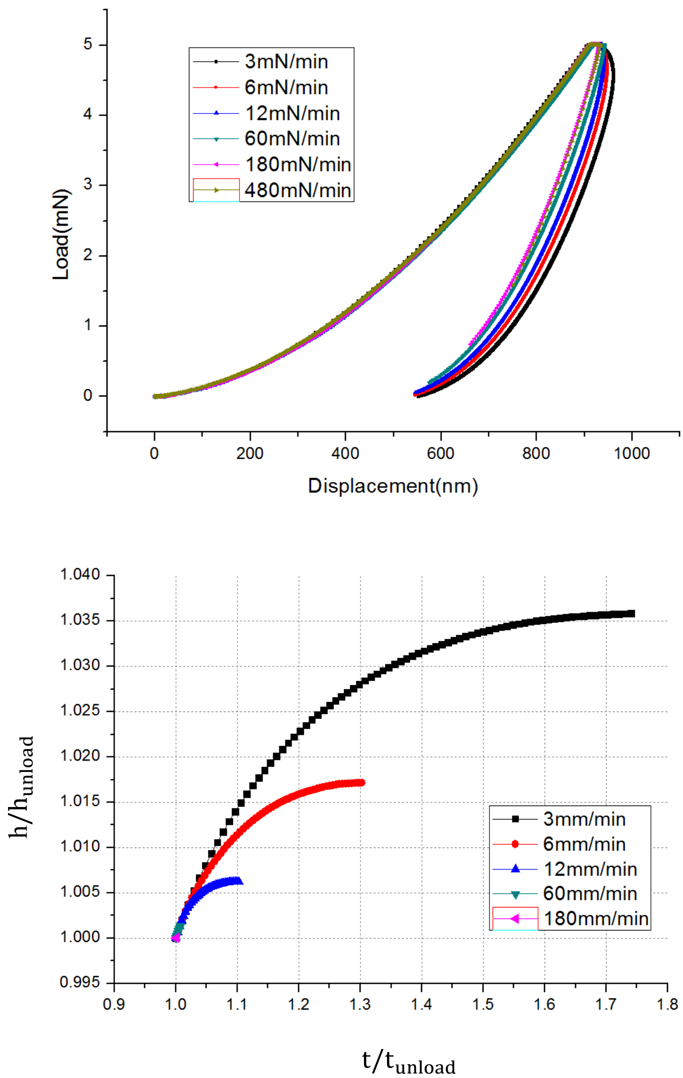
Figure 3.6. Load-displacement curve at different loading rates and the increments of displacement after unloading start





- Material: PMMA
- Maximum load: 5mN
- Loading rate: 30mN/min
- Hold time: 1s, 10s, 30s, 60s, 180s
- Unloading rate:3mN/min

Figure 3.7. Load-displacement curve at different hold times and the increments of displacement after unloading start



- Material: PMMA
- Maximum load: 5mN
- Loading rate: 30mN/min(specified)
- Hold time: 1s
- Unloading rate:3, 6, 12, 60, 180, 480mN/min

Figure 3.8. Load-displacement curve at different unloading rates and the increments of displacement after unloading start

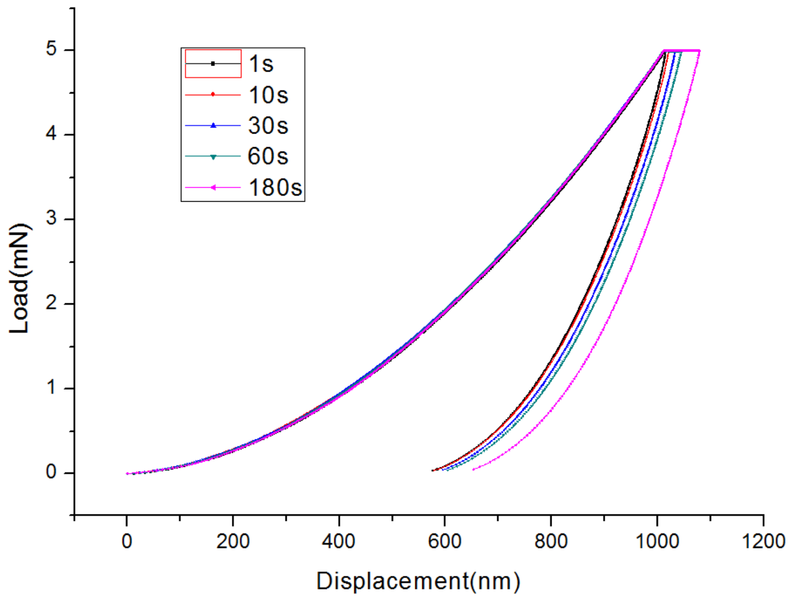


Figure 3.9. Load-displacement curve at different hold times with 1mN/min loading rate at which the nose phenomenon doesn't appear

3.3.2 Criterion for the Viscous Effect on Unloading Curve

It is important to establish a criterion for the viscous effect on the unloading curve in that the elastic modulus has its validity when the unloading curve is not bothered by the viscous effect. Especially, a significance of this criterion increases at slow unloading rates because the viscous effect is getting stronger. In order to establish a reasonable hypothesis for the criterion, we proceed with the interpretation of viscoelasticity from a molecular point of view. Viscoelasticity is specifically the reflection of a molecular rearrangement. When stress is applied, polymer chains entangle, untangle and slip each other like viscous liquid and a back stress occurs in the material due to the cohesion of great length of polymer chains like elastic solids. [32] The former is an operation of viscous component and the latter is that of elastic component.

Let's apply this unique behavior to the indentation process. In the loading process, molecular chains are rearranging their position by applied force and they continue their movements by the viscous component even when the peak load is reached because rearrangement is a time-consuming process. Based on this knowledge, one can think that time-dependent deformation, i.e. retarded deformation, no longer occurs when the retarded deformation rate by the viscous components and recovery rate by the elastic component which are opposite direction are the same. In the indentation process, this means when the “nose” disappears from the unloading curve. From this, Hypothesis I is established.

Hypothesis I

Viscous effect on unloading curve will be removed when the “nose” disappears.

This hypothesis is quite reasonable because the disappearance of the nose phenomenon means that there is no more increase in displacement in the unloading curve. In other words, the material is superficially in the direction of recovery. The verification process is carried out in two ways.

Case I: When the nose appears and disappears on the unloading curve

I. Find the point where there is no increase in displacement on the unloading curve.
II. Obtain the stiffness below that point.
III. Analyze that the stiffness is either maintained or decreased.

It is expected that there is no viscous effect on the unloading curve if the stiffness values are maintained. From the previous loading rate controlled experiment in Figure 3.6, the above verification process is performed. The point where there is no increase in displacement on the unloading curve at each condition and stiffness below that point are represented in Table 3.1. As can be seen, the stiffness at each condition is slightly reduced but not constant.

Following is another way of the verification.

<u>Case Ⅱ: When the nose is not observed on the entire unloading curve</u>

I. Find out the loading rate condition where there is no increase in displacement on the unloading curve.
II. Along with the above conditions, increase the hold time which is expected to decrease the viscosity effect.
III. Obtain the stiffness and analyze that the stiffness is either maintained or decreased.

From the previous loading rate controlled experiment, we found that there is no increase in displacement on the unloading curve at 1mN/min loading rate. Along with this condition, experiments are performed increasing the holding time as given by Figure 3.9. The stiffness values are in Table 3.2. As can be seen, the stiffness value decreases as the hold time increases but, remains constant from the 30s hold time. Both of these verifications indicate that disappearance of the “nose phenomenon” cannot be the criterion of the viscous effect on the unloading curve. This is because the retarded deformation rate essentially remains on the unloading curve even if the material is superficially in the direction of recovery. Therefore, another hypothesis is established.

<u>Hypothesis II</u>

> Viscous effect on unloading curve will be removed
>
> when pure recovery occurs.

This is illustrated well in Figure 3.10. To find the point where pure recovery occurs, i.e., the point at which the retarded deformation rate is zero, we assume that displacement rate will be increasing constantly when pure recovery occurs. This is based on the idea that a material will behave constant manner corresponding to the unloading rate if there is no rate in the opposite direction. Figure 3.11 demonstrates this through dh/dt-t diagram at different loading rate and hold time experiments in Figure 3.6 and 3.7.

The verification process is as follows.

I. Find a section where the displacement rate increases constantly on the displacement rate-time diagram of Case Ⅱ in Hypothesis I

II. Determine the stiffness of that section.

III. Compare the result with Case Ⅱ in Hypothesis Ⅰ.

The displacement rate-time diagram of Case II in Hypothesis I is given by Figure 3.12. The point where the displacement rate increases constantly at each condition and stiffness below that point are represented in Table 3.3. The point is determined by differentiating the displacement rate-time diagram of Case II in Hypothesis I. When the value is around zero, the rate change would be constant. As can be seen from the table, the stiffness values are constant even though there is small error and interestingly the stiffness values in Hypothesis II are same with the saturated values in Hypothesis I. Therefore, from the result of the verification process, Hypothesis II is reasonable. Additionally, saturated stiffness can be considered as the value without viscous effect. In the next chapter, we will evaluate the elastic modulus at various unloading rates based on this criterion.

Loading rate	1mN/min	5mN/min	10mN/min	60mN/min	120mN/min
Stiffness (unload fit 40-98%)	**0.026**	**0.031**	**0.033**	**0.034**	**0.035**
stdev.	5.77E-05	5.77E-05	0.000152753	0.000351188	0.0002
Nose(5mN=100%)	100	95.3	93.4	91	91
Stiffness (unload fit 40-nose%)	**0.026**	**0.03**	**0.031**	**0.032**	**0.032**
stdev.	5.77E-05	5.77E-05	5.7735E-05	0	5.7735E-05

Table 3.1. The point where there is no increase in displacement on the unloading curve and the stiffness below that point

Hold time + Loading rate(1mN/min)	1s + 1mN/min	10s + 1mN/min	30s + 1mN/min	60s + 1mN/min	180s + 1mN/min
Stiffness (40-98%)	**0.026**	**0.025**	**0.024**	**0.024**	**0.024**
stdev.	0.000109	8.57E-05	7.48331E-05	5E-05	9.5743E-05

Table 3.2. Stiffness when the nose is not observed on the entire unloading curve

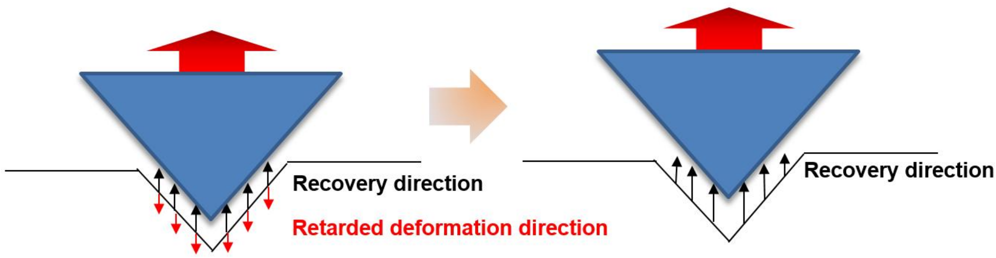


Figure 3.10. Difference between superficial and pure recovery

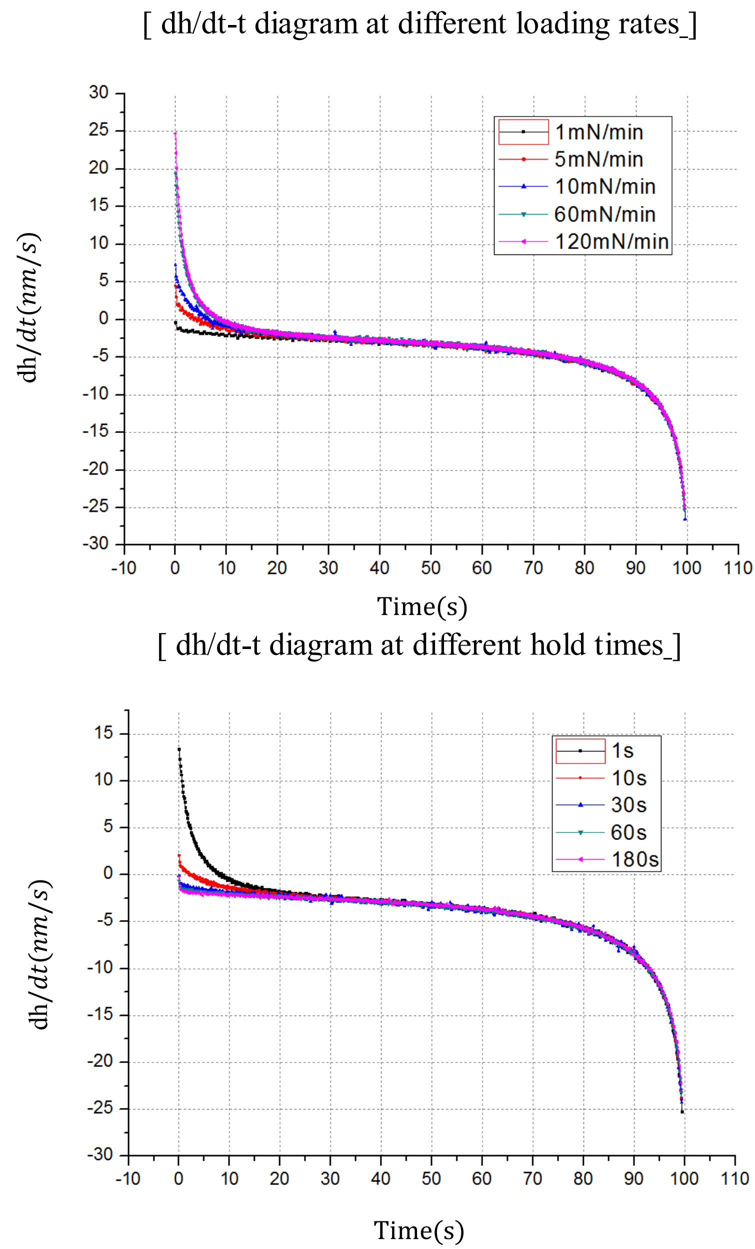


Figure 3.11. dh/dt-t diagram at different loading rate and hold time experiments

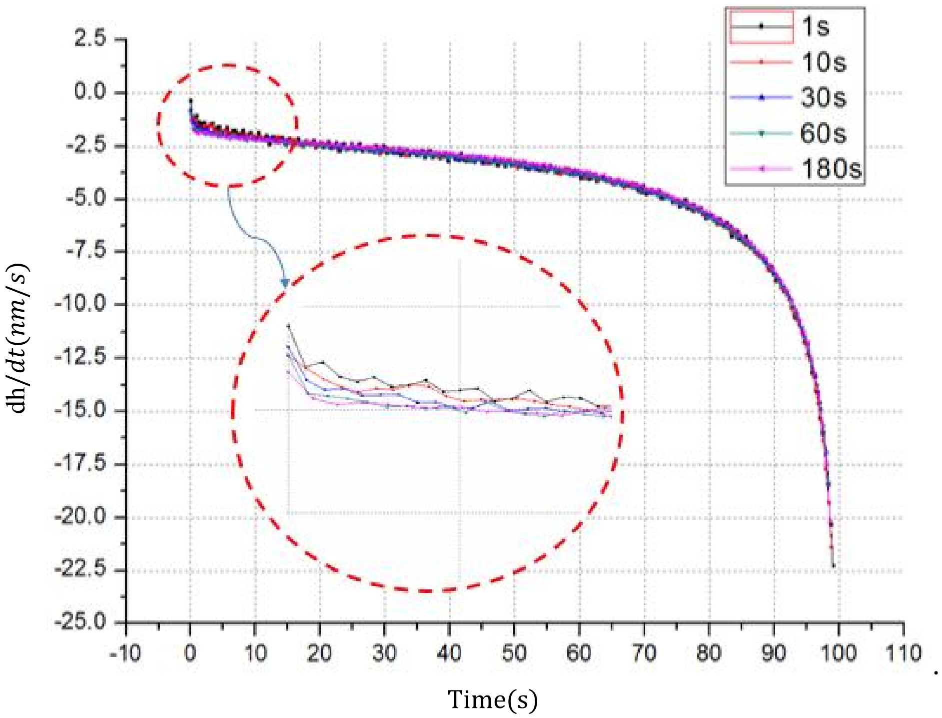


Figure 3.12. dh/dt-t diagram of CaseII in Hypotheisis I

Hold time + Loading rate(1mN/min)	1s + 1mN/min	10s + 1mN/min	30s + 1mN/min	60s + 1mN/min	180s + 1mN/min
Stiffness (40-98%)	**0.026**	**0.025**	**0.024**	**0.024**	**0.024**
stdev.	0.000108972	0.0001	5.7735E-05	5.7735E-05	0.00011547
Constant rate(5mN=100%)	86.1	86.4	87.2	88.6	89.1
Stiffness (unload fit 40-constant rate%)	**0.24**	**0.24**	**0.24**	**0.23**	**0.24**
stdev.	**5.7735E-05**	**5.7735E-05**	**0.00057735**	**5.7735E-05**	**0.000173205**

Table 3.3. The point where the displacement rate increases constantly and stiffness below that point

Chapter 4

Evaluation of Elastic Modulus at Various Unloading Rates

Contents

4.1 Introduction

As has been mentioned several times, the elastic modulus of polymeric materials has its importance when its dependence on time is realized. However, it is difficult to evaluate the elastic modulus of these materials by nanoindentation at various rates due to the operation of viscous component of viscoelastic materials. To solve this problem, in the previous chapter, the effective experimental method for reducing the viscous effect at slow unloading rates and the criterion for the viscous effect on the unloading curve are discussed. In this chapter, based on the experimental conditions satisfying the criterion, the elastic modulus at those conditions will be determined for three materials; PMMA, PC, ABS. These elastic moduli will be compared with those determined by a conventional experimental condition. Finally, the elastic moduli determined by nanoindentation test will be compared with those determined by tensile test for the verification. Further discussion will be followed.

4.2 Elastic Modulus at Various Unloading Rates

4.2.1 Experimental Details

The materials used in this paper are three amorphous thermoplastics: poly(methylmethacrylate) (PMMA), poly(carbonate) (PC), and poly(acrylonitrile-butadiene-styrene) (ABS). This type of polymers is selected because they show isotropic deformation which is expected to give more pronounced results to the viscous effect than semi-crystalline polymers expected to undergo anisotropic deformation.

All the nanoindentation tests are performed with an Ultra Nanoindentation Tester (UNHT, CSM Instruments by Anton Paar, Switzerland) with a Berkovich tip as illustrated in Figure 3.14. The maximum load for all experiments is 5mN, which corresponds to a depth slightly greater than 1 um for all specimens. This condition is determined to exclude an indentation size effect of elastic modulus(see Figure 3.15.)[33] Loading rate and hold time at peak load are determined for each specimen based on the criterion in Chapter 3. Along with these predetermined conditions, experiments are performed at 5 unloading rates(3, 6, 12, 60, 180mN/min) to evaluate the elastic modulus at various rates. For comparison, the experiment is repeated with 10s loading rate and 1s holding time according to the conventional Oliver and Pharr experimental condition. [12]

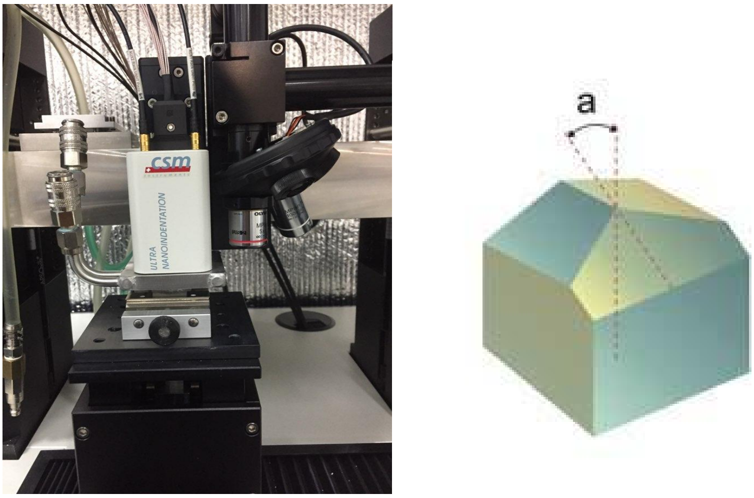


Figure 4.1. an Ultra Nanoindentation Tester (left) and a Berkovich indenter with a half angle ‘a’(right)

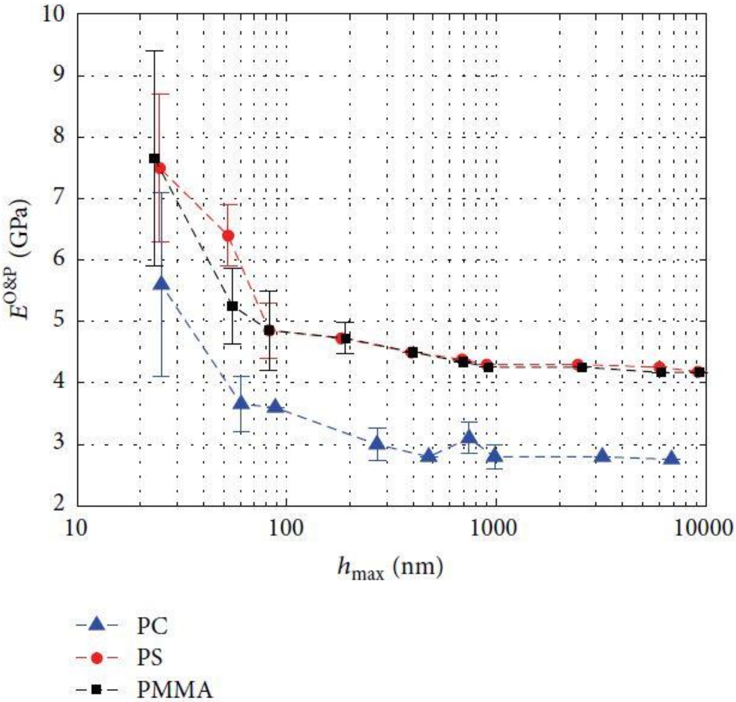
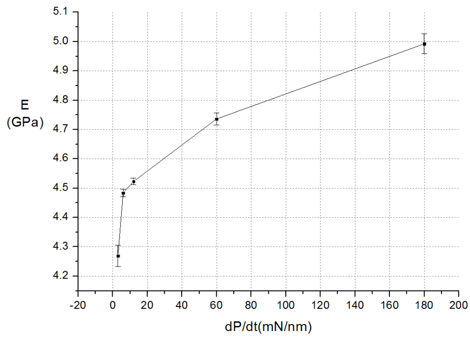


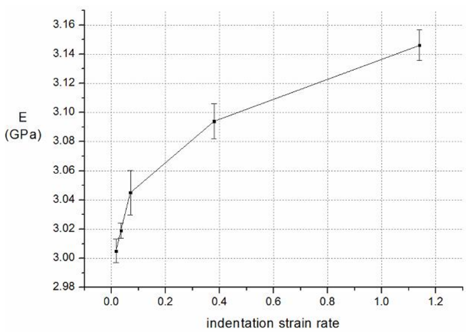
Figure 4.2. an indentation size effect of elastic modulus of polymeric materials [33]

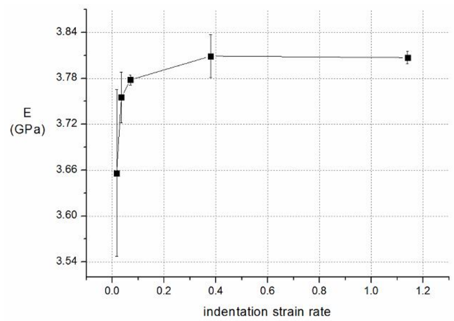
4.2.2 Elastic Modulus at Various Unloading Rates

The experimental conditions satisfying the criterion in Chapter 3 for each material are as follows: 1) PMMA: loading rate 1mN/min, hold time 30s 2) PC: loading rate 1mN/min, hold time 60s 3) ABS: loading rate 1mN/min, hold time 30s. These are based on the lowest unloading rate. Along with these predetermined conditions, experiments are performed at 5 unloading rates(3, 6, 12, 60, 180mN/min) for each material. As a matter of fact, it is possible to have a higher loading rate and a shorter holding time as the unloading rate increases. This is theoretically because recovery rate become much faster than the retardation rate as unloading rate increases. For the sake of convenience, however, the experiment is conducted under the same experimental conditions determined at the lowest unloading rate. The results are shown in Figure 4.3. As can be seen, the elastic modulus increases with increasing unloading rate in all materials. The reason of this is well explained in Section 2.3.3.



(a)





(b) (c)

Figure 4.3. Elastic modulus at 5 unloading rate conditions for each material.: (a) PMMA (b) PC (c) ABS

4.2.3 Comparison with Conventional Experimental Condition

As mentioned in 3.2.2, the conventional Oliver and Pharr method also considers the viscous effect on the unloading curve through the analytical method. However, that method is not sufficient to just adopt to polymeric materials because it is proposed based on the results obtained from materials such as metal and ceramic. Polymers have a unique molecular structure and it leads to a larger viscosity than the materials which have long-range ordered atomic structure. Therefore, the effective experimental method for reducing the viscous effect and the criterion for the viscous effect on the unloading curve for these materials are proposed in Section 3.3. The difference between the elastic moduli satisfying this criterion and those determined by the conventional experimental condition of Oliver Pharr method will be clarified through the various unloading rate experiments. It is expected that the importance of controlling the viscous effect on the unloading curve for polymeric materials will be revealed. The interesting results for three materials are shown in Figure 4.4, 4.5 and 4.6. As can be seen, the trend of the elastic modulus to the unloading rate is reversed. Also, the slower the unloading rate, the greater the gap. This clearly demonstrates the importance of controlling the viscous effect on the unloading curve for polymeric materials. This effect changes not only the magnitude but also the trend. In the next section, which trend is corrected one or not is verified.

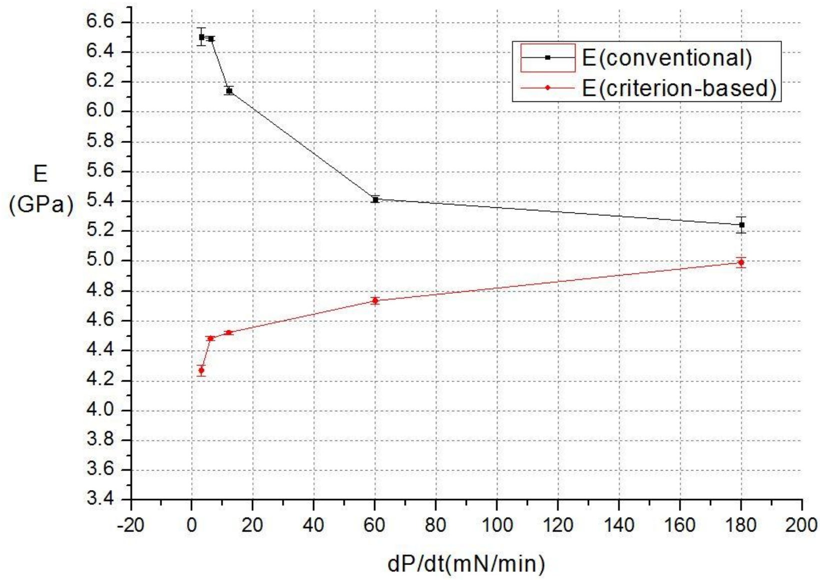


Figure 4.4. Comparison of elastic modulus determined by conventional and criterion-based experimental condition (PMMA)

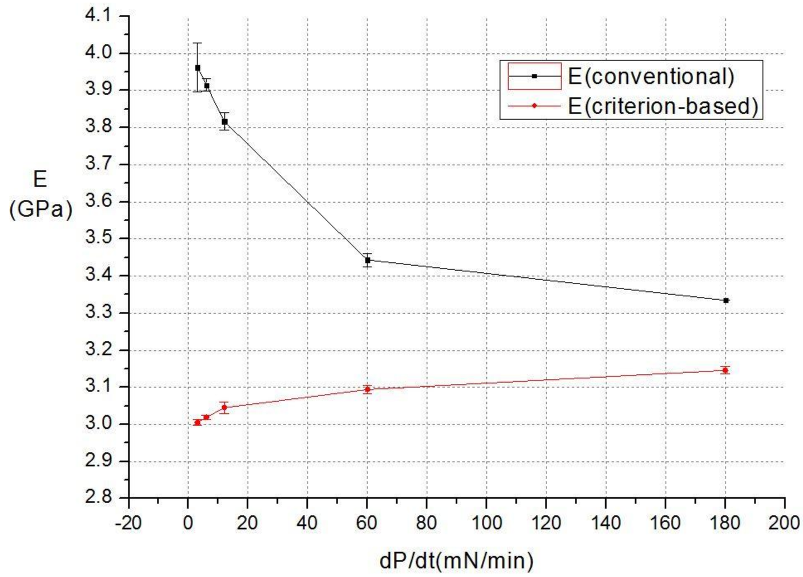


Figure 4.5. Comparison of elastic modulus determined by conventional and criterion-based experimental condition (PC)

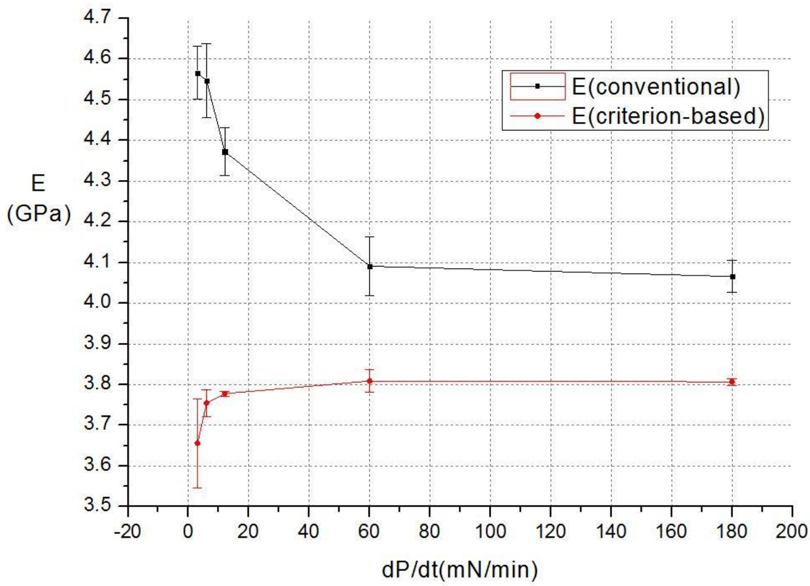


Figure 4.6. Comparison of elastic modulus determined by conventional and criterion-based experimental condition (ABS)

4.3 Verification Process

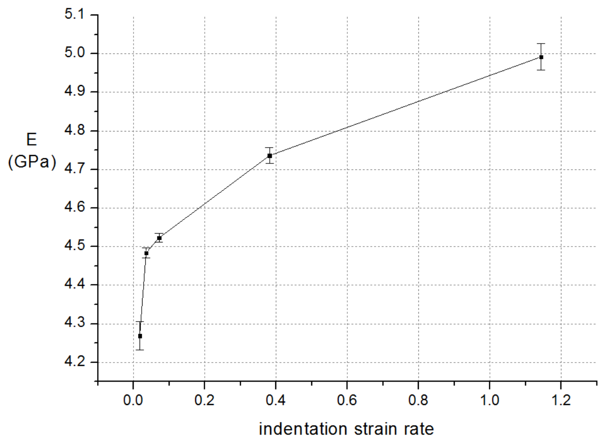
Elastic modulus at various unloading rates were determined using the criterion of viscous effect and compared with those determined by a conventional experimental condition. To verify these results, tensile tests are performed at various speed conditions. It is expected that both nanoindentation and tensile tests represent similar results.

4.3.1 Experimental Details

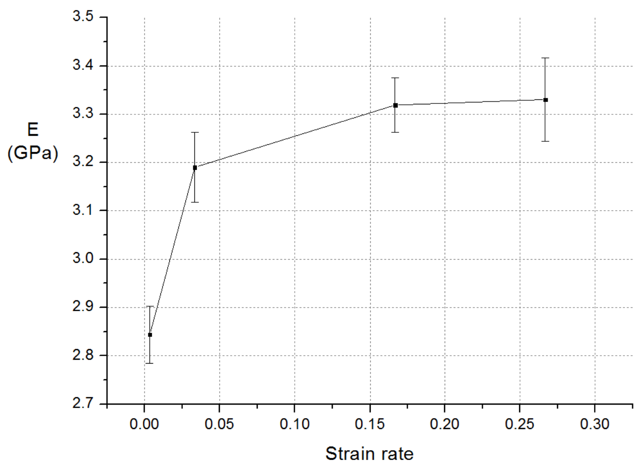
Tensile tests are performed with a universal testing machine(MTS, USA). Test condition and specimen size follow the ASTM standard for tensile properties of plastics.[8] Experiments are carried out at 4 testing speed conditions: 5, 50, 250, 400mm/min.

4.3.2 Comparison with Elastic Modulus determined by Tensile Test

It is important to obtain credible results of tensile test. To do so, ASTM standard is used to measure the tensile properties of polymers. The ASTM standard [8] specifies test conditions and adequate analysis methods for polymeric materials. Among those properties, elastic modulus is determined from the slope of the linear portion of the stress-strain curve which is calculated by dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain as indicated in Eq. (2-1). Because the exact stress-strain characteristics of polymer are highly dependent on rate of application of stress, standard recommended to evaluate the elastic modulus at various testing speeds. Figure 4.7, 4.8 and 4.9 illustrate the results of nanoindentation and tensile tests. As expected, they demonstrate similar results.

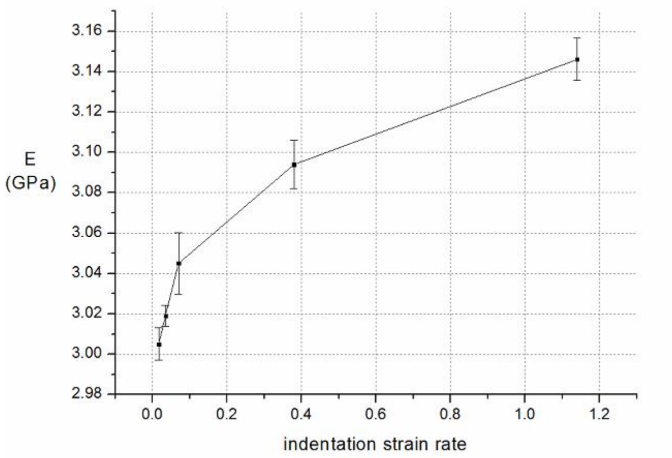


(a)

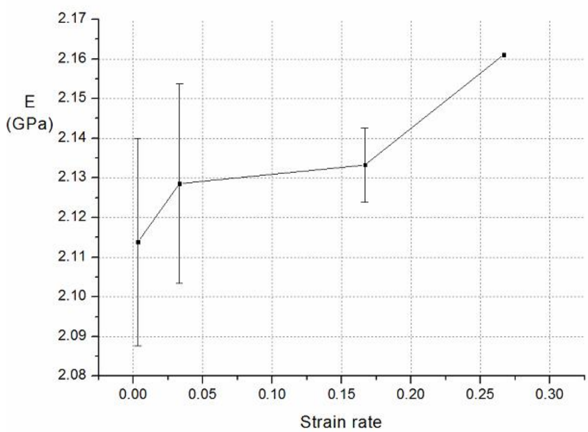


(b)

Figure 4.7. Comparison of elastic modulus determined by nanoindentation and tensile tests (PMMA)

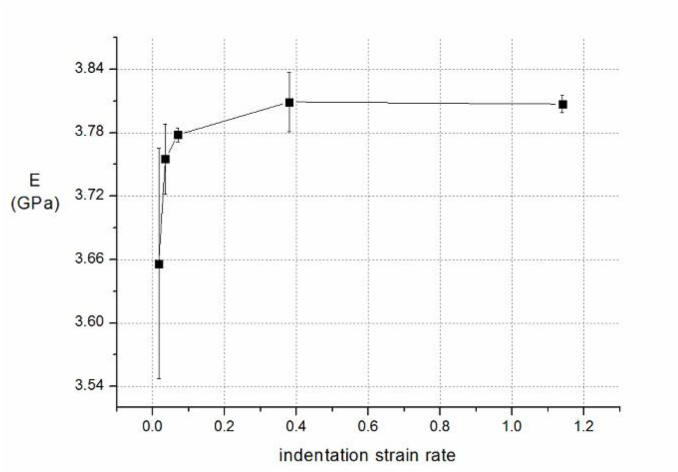


(a)

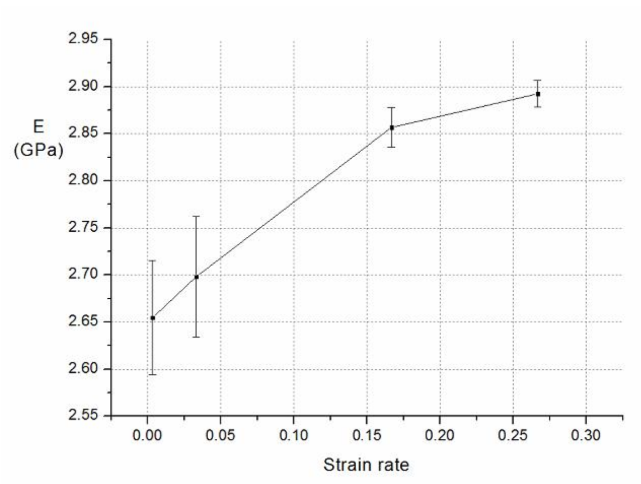


(b)

Figure 4.8. Comparison of elastic modulus determined by nanoindentation and tensile tests (PC)



(a)



(b)

Figure 4.9. Comparison of elastic modulus determined by nanoindentation and tensile tests (ABS)

4.3.3 Overestimation of Elastic Modulus

Although the tendency of the elastic modulus to rate is similar in both tests, there still remains an issue. The exact amounts of elastic modulus are differed from each other. To be specific, nanoindentation results overestimate those of tensile test. One can think that it could be an effect of rate. It means that the difference of rate in both tests derives the difference of the results. To find the answer of this, the rates of nanoindentation and tensile test should be corresponded and then compared. However, there is yet no way to correspond them. Despite this situation, the reason why there is an overestimation, the lowest elastic modulus at nanoindenation test is much higher than the highest elastic modulus at tensile test. To compare this schematically, the average values of elastic modulus at entire rate conditions are demonstrated in Figure 4.10, 4.11, and 4.12. As can be seen, elimination of viscous effect is effective for decreasing the elastic modulus, but it seems not enough. Therefore, various experimental and theoretical reasons have been suggested by many researchers. Specifically, A zero-point, hydrostatic pressure[34, 35], pile up[34,36] and tip calibration material[37] etc. are appointed to the reason of overestimation.

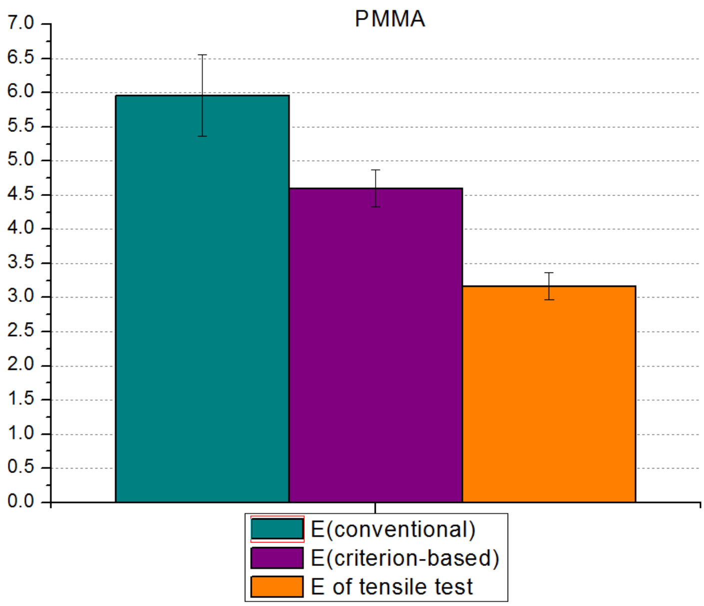


Figure 4.10. Comparison of average values of elastic modulus over the entire rate conditions (PMMA)

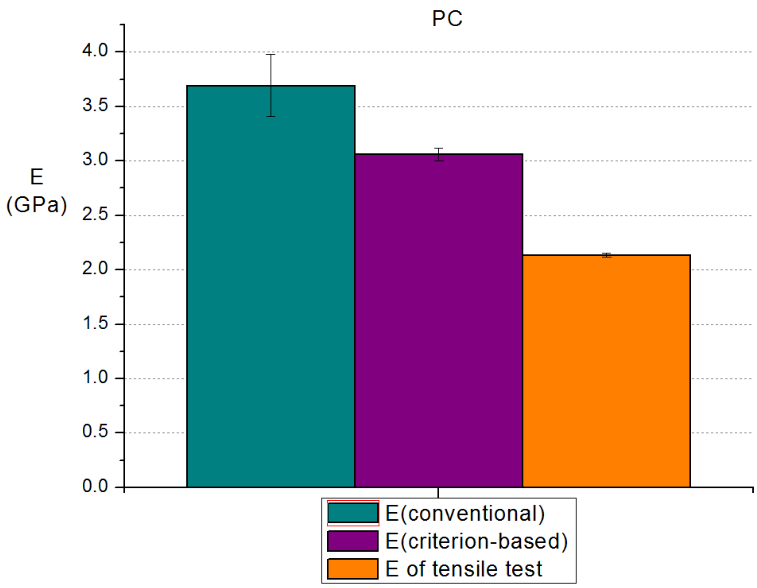


Figure 4.11. Comparison of average values of elastic modulus over the entire rate conditions (PC)

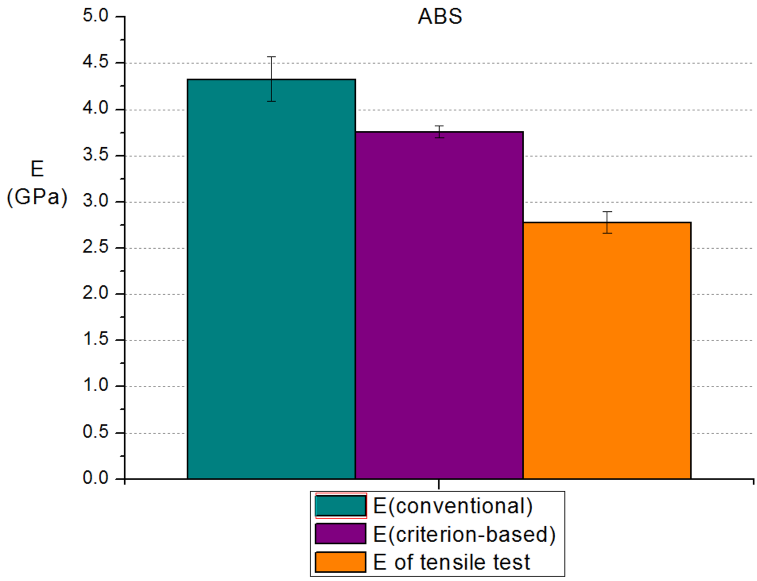


Figure 4.12. Comparison of average values of elastic modulus over the entire rate conditions (ABS)

Chapter 5

CONCLUSIONS

This study deals with the evaluation of elastic modulus of polymeric materials by nanoindentation test. The elastic modulus of these materials depends on time and thus we put emphasis on evaluating the elastic modulus at various rates. However, the abnormal indentation curve, called “nose” in the text, is an obstacle to achieve this goal. In order to interpret the information given by the abnormal indentation curve of these materials, understanding of mechanical behavior of polymer was preceded from the viewpoint of material structure.

Viscoelastic behavior, especially viscous one, is the root of this study. This unique behavior is the main reason of abnormal load-displacement curve, specifically unloading part of the curve from which the elastic modulus is determined. The distortion of the curve gets more serious when the rate is slower. Therefore, in this study, we suggested experimental parameters and conditions in which viscous effect on unloading curve can be effectively reduced at the slow unloading rates.

In addition, we investigated the criterion which can be used to discriminate whether the viscous effect on the unloading curve is eliminated or not. Based on this criterion, the modulus of elasticity of the polymeric material was evaluated at various unloading rates without viscous effect on unloading curve. It was revealed that the trend of the modulus of elasticity with respect to unloading rate is reversed when it compared to the results of the conventional experimental condition.

For verification, the comparison with the elastic modulus determined by tensile test was carried out and it was confirmed that the trend of the elastic modulus was well matched with that of the elastic modulus satisfying the criterion.

[1] Jenn Stroud Rossmann, *Introduction to Engineering Mechanics: A Continuum Approach, Second Edition* p.35. (CRC Press, 2015)

[2] Sadd, Martin H., *Elasticity: Theory, Applications, and Numerics*. Oxford: Elsevier. P. 70. (2005)

[3] Donald R. Askeland, Wendelin J. Wright, *Science and Engineering of Materials, SI Edition,* (Cengage Learning, 2015)

[4] Joachim Roesler, Harald Harders, Martin Baeker, *Mechanical Behaviour of Engineering Materials* p.270. (Springer Science & Business Media, 2007)

[5] Herbert Baur, *Thermophysics of Polymers I : Theory*(Springer Science & Business Media, 2012)

[6] David Roylance, *Engineering viscoelasticity,* Dep. Mater. Sci. Eng. Inst. Technol. Camb. MA (2001)

[7] N. Aleksy, G. Kermouche, INT J MATER FORM (2010)

[8] ASTM Test Method D638: *Standard Test Method for Tensile Properties of Plastics* (2014)

[9] Meyers, M.A.; Chawla K.K. *Mechanical Behavior of Materials*. Prentice-Hall (1999)

[10] ASTM Test Method E2546: *Standard Practice for Instrumented Indentation Testing* (2007)

[11] M.F. Doerner and W.D. Nix, J. Mater. Res. 1, (1986)

[12] W.C. Oliver and G.M. Pharr, J. Mater. Res. 7, (1992)

[13] W.C. Oliver and G.M. Pharr, J. Mater. Res. 19, (2004)

[14] D. Tabor, *The Hardness of Metals*, Clarendon Press (1951)

[15] Anthony C. Fischer-Cripps, *Nanoindentation 2nd Edition,* (Springer Science & Business Media, 2004)

[16] Hertz, H., *Uber Die Beruhrung Fester Elastischer Korper (on the contact of elastic solids)*, J. Reine Angew. Math., 156–171 (1881)

[17] Boussinesq, J., *Applications des Potentials a l'Etude de l'Equilibre et du Mouvement des Solides Elastiques*, (1885)

[18] Sneddon, I.N., *Boussinesq's problem for a rigid cone,* Proc. Cambridge Philos. Soc., 492–507 (1948)

[19] King, R.B., *Elastic analysis of some punch problems for a layered medium*, Int. J. Solids Struct. 23, 1657–1664 (1987)

[20] Alexander Ya. Malkin, Avraam I. Isayev, *Rheology: Concepts, Methods, and Applications*, p.43-44. (Elsevier, 2017)

[21] Robert O. Ebewele, *Polymer Science and Technology,* p.402. (CRC Press, 2000)

[22] Meyers and Chawla, *Mechanical Behavior of Materials*, p.98-103. (1999)

[23] Ton van Vliet, *Rheology and Fracture Mechanics of Foods*, p.65-66.

(CRC Press, 2013)

[24] AHW Ngan, B Tang, *Viscoelastic effects during unloading in depth-sensing indentation,* J. Mater. Res. 17, 2604-2610 (2002)

[25] B Tang, AHW Ngan, *Accurate measurement of tip–sample contact size during nanoindentation of viscoelastic materials,* J. Mater. Res. 18**,** 1141-1148 (2003)

[26] Donna M. Ebenstein, Lisa A. Pruitt, *Nanoindentation of biological materials,* Nanotoday*,* 1, 26-33 (2006)

[27] C.Y. Zhang, Y.W. Zhang, K.Y. Zeng, L. Shen, *Nanoindentation of Polymers with a Sharp Indenter,* J. Mater. Res. 20**,** 1597-1605 (2005)

[28] Chien-Chao Huang, Mao-Kuo Wei, Sanboh Lee, *Transient and steady-state nanoindentation creep of polymeric materials,* Int. J. Plast., 27, 1093-1102 (2011)

[29] Matthieu Vandamme, Franz-Josef Ulm, *Viscoelastic solutions for conical indentation,* Int J Solids Struct. 43, (2006)

[30] Cheng, Y. T.; Cheng, C. M. J. *Relationships between initial unloading slope, contact depth, and mechanical properties for conical indentation in linear viscoelastic solids,* J. Mater. Res., 20, 1046-1053 (2005)

[31] B J Briscoey, L Fiori and E Pelillo, *Nano-indentation of polymeric surfaces,* J. Phys. D: Appl. Phys., 31 (1998)

[32] N. G. McCrum, C. P. Buckley, C. B. Bucknall, *Principles of Polymer Engineering,* 117 (Oxford University Press, 1997)

[33] Farid Alisafaei, Chung-Souk Han, *Indentation Depth Dependent Mechanical Behavior in Polymers,* Adv. Cond. Matter Phys., 2015, 20 (2015)

[34] M. Hardiman, T.J. Vaughan. C.T.McCarthy, *The effects of pile-up, viscoelasticity and hydrostatic stress on polymer matrix nanoindentation,* Polymer Testing, 52, 157-166 (2016)

[35] Angel Strojny, Xinyun Xia, Andy Tsou & William W.Gerberich *Techniques and considerations for nanoindentation measurements of polymer thin film constitutive properties,* Adv. Cond. Matter Phys., 12:12, 1299-1321 (1998)

[36] Davide Tranchida, Stefano Piccarolo, Joachim Loos, *Mechanical Characterization of Polymers on Nanometer Scale through Nanoindentation. A Study on Pile-up and Viscoelasticity,* Macromolecules., 40,1259-1267(2006)

[37] B.J.Briscoe, L Friori, E Pelillo, *Nano-indentation of polymeric surfaces,* J. Phys. D: Appl. Phys., 31, 2395-2405 (1998)

초 록

폴리머 재료의 탄성계수는 그것의 시간, 온도 및 기타 환경조건들에 대한 의존성이 밝혀 질 때 중요성을 나타낸다. 그 중에서도 점탄성이라고 알려진 시간의존 특성은 많은 연구자들에 의해 연구되어 왔다. 이러한 시간의존 특성을 명확히하기 위해서는 다양한 속도에서의 탄성계수를 구할 필요가 있다.

나노압입기술은 인장시험, 동적기계적 분석법과 함께 시간의존적인 탄성계수를 평가하는데 사용되는 유용한 방법 중 하나이다. 이 기술은 이름상에 명시된 바와 같이 작은 크기 범주를 가지는 재료에 대해 평가가 가능하다는 점에서 그 이점을 갖는다.

나노압입시험에서 탄성계수는 하중을 가하는 과정에서 변형되었던 재료가 원상태로 복원하려는 성질을 나타내는 하중 제거 과정의 언로딩 곡선을 통해 구할 수 있다. 하지만, 점탄성을 가지는 재료의 경우에는 재료가 하중이 제거되는 과정 중에 순수한 복원만 일어나는 것이 아니라 하중이 가해지던 방향으로 변형하려 하기 때문에 결과적으로 하중-변위 곡선의 모양을 변화시키게 된다. 이는 언로딩 곡선에서 볼록한 모양을 나타내기 때문에 “코”라고 불린다. 이에 따라, 언로딩 곡선의

기울기인 강성도가 변하게되고 그로인해 탄성계수 또한 변하게 된다. 이것은 가역과정 동안 인가된 힘에 의해 유도된 재료의 점성 거동에 의한 결과라고 할 수 있다.

따라서, 다양한 속도에서의 탄성계수를 구하려는 목적을 달성하기 위해서 본 연구에서는 낮은 언로딩 속도에서 점성 효과를 효과적으로 감소시키는 실험적 요소와 조건들을 나타낸다. 또한, 언로딩 곡선 상에서는 점성효과가 제거되었는지 아닌지를 판별할 수 있는 기준에 대해 조사한다. 결정된 기준에 근거하여 폴리머 소재의 탄성계수를 정성효과가 사라진 상태에서 다양한 언로딩 속도상에서 평가하고 기존 실험 조건으로 실험한 경우와 그 값을 비교한다. 최종적으로, 검증을 위해 인장시험으로 구한 탄성계수와의 비교를 진행한다.

주요어: 탄성계수; 나노압입시험; 폴리머; 저속; 점탄성; 점성 거동

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