An Unexpected Plasticization Phenomenon and a Constant of the Change Rate of Viscoelastic Properties for Polymers During Nanoindentation Test

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ABSTRACT: The effect of loading force, loading rate and unloading rate on the viscoelastic behavior of three representative polymers: poly(methyl methacrylate) (PMMA, amorphous polymer), polyvinylidene fluoride (PVDF, semicrystalline polymer), and epoxy (crosslinked polymer) have been investigated using nanoindentation. The results showed that the maximum indentation depth increased with the increase of loading force, and the relationship between loading force and depth became linear when the loading force is beyond 3000 μN. At the beginning, the plasticity index changed substantially with the increase of loading force, and after reaching a critical loading force, the plasticity index almost remained constant. The maximum indentation depth decreased with the increase of loading rate, which followed a power law curve. With the increase of loading rate, a plasticization phenomenon happened, and a possible reason is that the heat may accumulate and raise the local temperature. The plasticity index initially followed the power law with the increase of unloading rate and then almost remained constant. A constant, the change rate of viscoelastic properties with the unloading rate, for the three representative polymers studied in this research, around −0.033, has been obtained, which may be another manifestation of the phenomenon that many polymers have similar time/temperature shifts and that their WLF equation constants are approximately the same. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 885–890, 2011

Key words: nanoindentation; viscoelastic behavior; plasticization

INTRODUCTION

Nanoindentation has been proven to be an effective and convenient method to determine the mechanical properties of solids, most notably, elastic modulus and hardness. The method is based on the analysis of the unloading load–displacement response which is assumed to be elastic, even if the contact is elastic–plastic, which means plasticity occurring instantaneously upon satisfaction of a constitutive criterion and that there are no time-dependent effects.[1,2] A typical nanoindentation test provides load-depth data, which are the deformation responses of a material.[3,4] The possibility to test thin films, coatings, and small structures, as well as the possibility of mapping mechanical properties and subsequently to link them to morphology and processing conditions, makes the nanoindentation test a fundamental tool in polymer science.[5–9]

However, the use of nanoindentation for nanoscale mechanical characterization of polymers is hampered by the principal assumption of most theories that the behavior of the material during unloading is elastic only, while actually for most polymers and testing conditions, it is strongly influenced by viscoelasticity.[5,10] Cheng et al.[11,12] showed that the Oliver and Pharr method cannot be used to correctly evaluate the contact area in the presence of the viscoelastic deformation. Ngan et al.[13,14] and Cheng et al.[11,12] have proposed novel procedures to determine the initial unloading slope, which can be reliably applied to both linearly viscoelastic materials and nonlinear viscoelastic materials. Their results showed that fast unloading is essential in determining the instantaneous modulus from initial unloading slope too. It is obvious that the visoelastic behavior is related with the test procedure, which makes the research on the viscoelastic behavior of polymer during nanoindentation test become an important

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topic. It not only contributes to the application for nanoindentation testing of polymers, but also provides important information about polymer viscoelastic behavior, especially on the nanoscale.

Tranchida et al.[15] reported the viscoelastic recovery behavior following atomic force microscope nanoindentation of semicrystalline poly(ethylene) and showed that the recovery after 24 h was substantial, although not completed. Moreover, the dynamics of the recovery process was not seen to depend on the magnitude of the applied load for the nanoindentation, but instead on the rate of the indentation used. Wornyo et al.[16] studied shape memory polymer networks by nanoindentation and examined the small-scale deformation and thermally induced recovery behavior of shape memory polymer networks as a function of crosslinked structure. Zhou et al.[17] studied the surface and interface viscoelastic behaviors of thin polymer films by nanoindentation and reported the existence of three regimes of different viscoelastic behaviors demonstrated by the stiffness variation across the film. They also studied the nanoscale plastic deformation and fracture of polymers by *in situ* nanoindentation. The study of the indentation-induced plasticity during loading and the significant recovery of the deformed polymer upon unloading provided the insight into the nanoscale viscoelastic and plastic behavior. This study also provided information on the evolution of nanoscale viscoelastic–plastic deformation and fracture–delamination processes at polymer surfaces during the loading and unloading phases of a nanoindentation cycle.[18]

In previous research, most works just focus on one type of polymer. However, in this research, the nanoscale deformation and recovery behavior of three representative polymers: poly (methyl methacrylate) (PMMA, amorphous polymer), polyvinylidene fluoride (PVDF, semicrystalline polymer), and epoxy (crosslinked polymer) were investigated by nanoindentation to highlight the inherent phenomena of the polymer viscoelastic behavior and to help understand the application of nanoindentation in nanoscale mechanical characterization of polymers.

EXPERIMENTAL

Materials

The materials used in this study were three representative commercial polymers, including PMMA (amorphous polymer, Altuglas, Arkema, commercial product), PVDF (semicrystalline polymer, Kynar 741, commercial product), and epoxy (crosslinked polymer, LECO, produced according to the recommendation procedure).

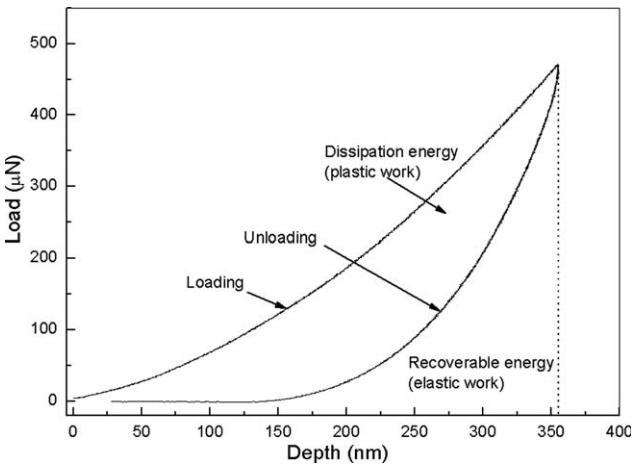

Figure 1 Representative nanoindentation curves of the load and unload-depth curve (this curve is from PVDF).

Nanoindentation

Nanoindentation tests were performed on a TriboIndenter (Hysitron, USA). A Berkovich diamond indenter of tip radius of 100 nm was used. Before the test, the air indent calibration, tip area function calibration, and machine compliance calibration have been done on fused silica. In-built function of the instrument to measure and correct the drift has been applied. The resolutions of the loading and displacement of the systems are 1 nN and 0.002 nm, respectively. All the tests were conducted at room temperature (25°C ± 1°C). At least three points have been done, and if the repeat is not good, more points have been test until a reasonable data have been obtained. Indentations have been performed in a wide range of experimental conditions. Seven different loading force (500, 1000, 2000, 3000, 4000, 5000, and 8000 μN), six loading rates (20, 50, 200, 500, 1000, and 2000 μN/s), and six unloading rates (20, 50, 200, 500, 1000, and 2000 μN/s) were used.

Figure 1 shows the representative nanoindentation curves. During indentation, the applied load and the tip displacement are continuously recorded. From such data, mechanical properties, such as the elastic modulus or the yield stress of the materials, can be extracted using various methods, depending on the deformation regime and tip geometry. In all indentation analysis models, the estimated accuracy of mechanical properties is strongly related to an accurate determination of the contact between the indenter tip and the material surface.[19] The contact mechanics become very important, and a lot of researches have been done and some theoretical models on the rate effects of contact mechanics for viscoelastic solids have been put forward.[20–26]

To simplicity, in this research, we use the plasticity index to quantify the visoelastic properties of the polymer. The plasticity index, ψ, of a solid body is

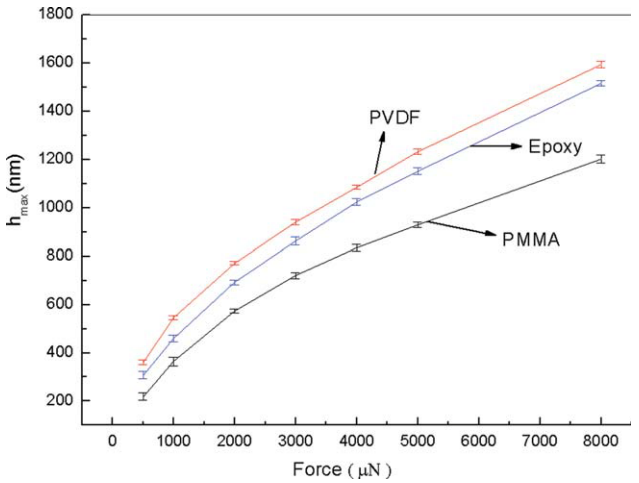

Figure 2 The effect of loading force on the maximum depth (loading rate, 200 N/s, unloading rate, 200 N/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

usually used to characterize the relative plastic/elastic behavior of the material when it undergoes external stresses and strains. For the case of polymeric material, one of the definitions for the plasticity index is the ratio of the area encompassed between the loading and unloading curves (equals to plastic work and other loss terms such as internal friction during the indentation) to the total area encompassed under the loading curve (total work including the plastic work and viscoelastic recovery). It follows that $\psi = 1$ for a fully plastic deformation, $\psi = 0$ for a fully elastic case, and $0 < \psi < 1$ for viscoelastic–plastic behavior.[27–29]

RESULTS AND DISCUSSION

Effect of the loading force

Figure 2 shows the effect of loading force on the maximum depth. It can be seen that the maximum depth increased with the increase of loading force. It is easy to understand that the higher the force, the larger the deformation, and thus the larger the penetration depth. Another phenomenon was that the maximum depth increased linearly with the increase of the loading force when the loading force was over 3000 μN. In the loading range between 3000 and 8000 μN, the slope for PMMA was 0.095 (±0.003) and the linear regression coefficient (R^2) was higher than 0.998. For PVDF and epoxy, the slopes were 0.129 (±0.004) and 0.128 (±0.005), respectively, and the linear regression coefficient (R^2) both were higher than 0.996. The linear relationship between load and penetration after the very first region of the loading force curve is very interesting, and especially this phenomenon is observed for all three representative polymers. The reason for this is not clear yet, and more detail research for this will be investigated in future work.

Figure 3 shows the effect of the loading force on the plasticity index. It is obtained that at the beginning the plasticity, index changed substantially with the increase of loading force, but after reaching a critical loading force, the plasticity index remained almost constant. The critical loading force in this research was 5000 μN for PMMA, 4000 μN for epoxy, and 3000 μN for PVDF. The reason for this may lay in the fact that the critical loading force corresponded to large deformation. For small deformation, there are many factors affecting the test results such as (1) surface macromolecules respond much faster to mechanical stimulus than bulk macromolecules because of less entanglement interactions in the near-surface region[17]; (2) properties of the polymer. For example, there are linear viscoelastic region, nonlinear viscoelastic region, yield, and even double yielding for some polymers during tensile test[30–36]; (3) the change of the contact area between indenter and the polymer.[37] That is why it is observed that plasticity index changed a lot during low-loading force stage (corresponding small deformation). However, all these factors will become negligible or almost remain constant during large deformation. In that situation, the deformation of polymers is mainly affected by the reduced mobility of the molecular chains (entanglement effect),[17] and the plasticity index almost remains constant.

Effect of the loading rate

The trend of the maximum depth for the three polymers used in this research decreased with the increase of loading rate, as shown in Figure 4, which

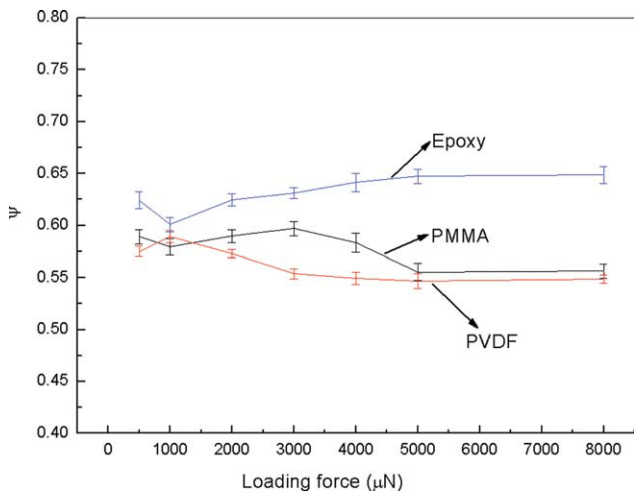

Figure 3 The effect of loading force on the plasticity index (loading rate, 200 N/s; unloading rate, 200 N/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

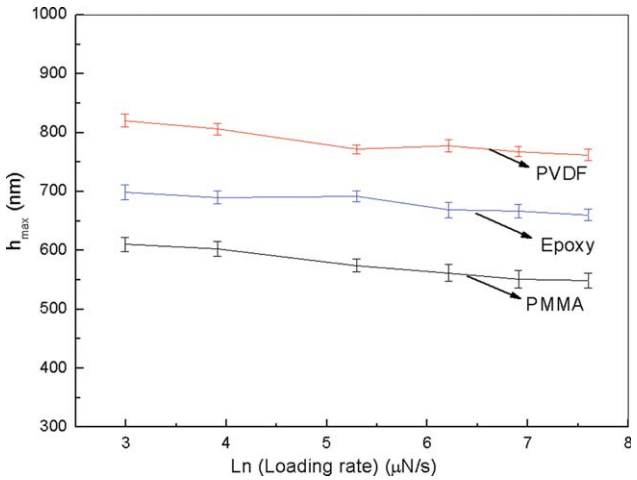

Figure 4 The effect of loading rate on the maximum depth (loading force, 2000 N, unloading rate, 200 N/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

followed the power law. Tranchida et al.[10] also reported the same trend for several poly(ethylene) samples with a broad range of morphologies.

Figure 5 presents the effect of loading rate on the plasticity index. It is interesting to note that the plasticity index increased with the increase of loading rate, which is against the observation obtained in tensile test. Normally, the viscoelastic behavior of a polymer is sensitive to the strain rate. For example, the study of the tensile deformation behavior of polymeric materials has been the subject of numerous investigations in a number of publications, and the extensive work has established that both the testing temperature and the strain rate are the crucial factors in determining the deformation characteristics of polymers.[38,39]

It is well known that the Eyring formalization[40] for thermally activated rate processes has been the most largely used model for clarifying the yield mechanism of glassy and semicrystalline polymers. A detailed investigation for the yielding behavior of PMMA and polycarbonate over a wide range of strain rates and temperatures by Roetling[41] and Bauwens[42] has shown that the yield stress increases more rapidly with increasing strain rate and decreasing temperature at low temperatures and high strain rates than at high temperatures and low strain rates.[38] Thus, it seems that the higher loading rate leads to higher strain rate, which should result in higher elasticity. However, in this work, the results showed that high loading rate did not lead to high elasticity, but on the contrary, high plasticity, at least for the three representative polymers used here, PMMA (amorphous polymer), PVDF (semicrystalline polymer), and epoxy (crosslinked polymer) are under the investigation condition in this research. The reason for this phenomenon is not clear yet.

A possible mechanism is that the plasticity is from the increase of the local temperature. It is known that the work expended in deforming and fracturing of the solid can be stored internally, used for generating new surfaces, or dissipated, usually in the form of heat. If some of the work is dissipated as heat and the deformation process is sufficiently transient, so that thermal conduction does not have time to occur, a local increase in temperature may occur.[43] Polymer dissipates heat much more slowly than metal.[44,45] So, during the test, the heat may accumulate and results in the increase of local temperature. As mention before, the deformation for polymer is sensitive to temperature, and so plasticity will happen. Higher loading rate means less time available for the heat dissipation, will lead more heat accumulation, and eventually result in higher plasticity index.

Effect of the unloading rate

Figure 6 demonstrates the effect of unloading rate on the plasticity index. For all three polymers studied here, the plasticity index initially followed power law with the increase of unloading rate and then almost remained constant. It can be seen that the plasticity index was sensitive to the unloading rate, which was indicative of the viscoelasticity of the materials during unloading process. This result further verified that indeed the use of nanoindentation for nanoscale mechanical characterization of polymers is hampered by the principal assumption of most work that the behavior of the material during unloading is elastic only, while actually for most polymers and testing conditions, it is strongly influenced by viscoelasticity.[5] And here, higher unloading rate and higher elasticity support the conclusion

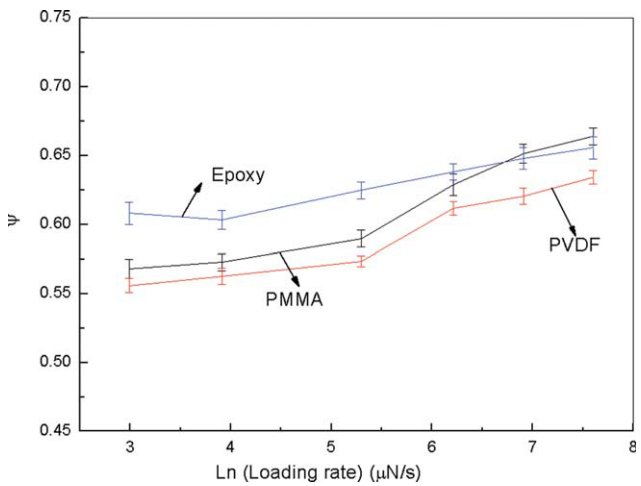

Figure 5 The effect of loading rate on the plasticity index (loading force, 2000 N, unloading rate, 200 N/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

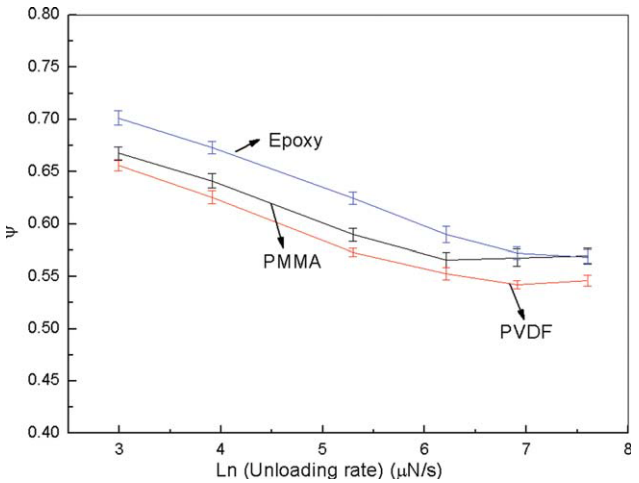

Figure 6 The effect of unloading rate on the plasticity index (loading force, 2000 N, loading rate, 200 N/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by Cheng et al.[11,12] that fast unloading is essential in determining the instantaneous modulus from initial unloading slope. The linear regression coefficient (R^2) of all three polymers was higher than 0.99. It was found that the slope (the change rate of viscoelastic properties with unloading rate) was −0.032 (± 0.001) for PMMA, −0.033 (± 0.002) for PVDF, and −0.033(± 0.001) for epoxy when the unloading rate was lower than 500 μN/s. It was interesting to note that the change rate of viscoelastic properties with unloading rate for the three so different kind of polymer in this research was almost the same, around −0.033.

During the loading process, elastic energy has been stored in the sample. Although this stored energy will have both a time-dependent and a time-independent component. Findley et al. and Goldman et al.[46–48] have reported that recovery after hydrostatic compression was complete and occurred very rapidly, practically simultaneously with the removal of the pressure. Although the deformation during indentation is somewhat different from hydrostatic compression, the deformation is largely compressive and constrained, and so it is probable that the stored elastic energy is released relatively quickly during unloading, that is, in the time frame of the unloading process. If this was not the case, then with increasing unloading rate, more of the time-dependent elastic energy would not be recovered during unloading, and the measured plasticity index would be higher than expected and increase with unloading rate. At the same time, other time-dependant viscoelastic behavior may occur during the unloading process, such as creep. At low unloading rates, the material is under high loads for a reasonable length of time, which allows time for further time-dependent elastic and plastic deformation to occur. This will increase the plasticity index at low unloading rates, but the effect will decrease with increasing unloading rate. If the sample is unloaded faster than the time required for the molecular relaxations to occur, then creep deflection will be very low, and the plasticity index will flatten out. So it can be obtained that for polymer, it is the creep behavior resulted from the hold force during unloading dominate the viscoelastic properties. It is interesting to note that the point where the plasticity index flattens out in Figure 6 depended on the type of polymer. It occurred at a higher rate for the epoxy than the PMMA, which is consistent with the more constrained large-scale molecular motions in the cross-linked epoxy than the linear PMMA. PVDF is a semicrystalline polymer, the chains of which in the amorphous regions are entangled and form a network, which acts together with the skeleton of lamellar crystallites, and both together hold the applied force,[49–51] and so the time dependence of its plasticity index levels out at an intermediate rate between the epoxy and the PMMA. The slope of the plasticity index versus log unloading rate is similar for the three polymers of this study. This may be another manifestation of the phenomenon that many polymers have similar time/temperature shifts and that their WLF equation constants are approximately the same.

CONCLUSIONS

A study of the viscoelastic behavior of three typical polymers, PVDF, PMMA, and epoxy, has been carried out by nanoindentation test. The main conclusions were as follows:

1. The maximum depth increased with the increase of loading force, and the relationship became linear when the loading force was beyond 3000 μN. In the beginning, the plasticity index changed significantly with the increase of loading force; however, after a critical loading force, the plasticity index almost remained constant.
2. The maximum depth for the three polymer materials decreased with the increase of loading rate, and the relationship between maximum depth and loading rate can be described using a power law. The plasticization phenomenon occurred during test, that is, the plasticity index increased with the increase of loading rate, and a possible reason for this phenomenon is that the heat may accumulate and result in the local temperature increase.
3. The plasticity index followed the power law with the increase of the unloading rate, and

then it almost remained constant, and the creep behavior resulted from the hold force during unloading dominate the viscoelastic properties during unloading process.

4. A constant, the change rate of viscoelastic properties with unloading rate for the three typical polymers used in this research, around −0.033, has been observed, which may be another manifestation of the phenomenon that many polymers have similar time/temperature shifts and that their WLF equation constants are approximately the same.

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