Article

Measurement of viscoelastic properties for polymers by nanoindentation

Yuemin Wang[1], Lei Shang[1], Panpan Zhang[2], Xiangqiao Yan[1], Ke Zhang[3], Shuliang Dou[1*], Jiupeng Zhao[3*] and Yao Li[1*]

[1] Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin, China
[2] Jincheng campus, Taiyuan University of Science and Technology，Jincheng, China
[3] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China
* Correspondence: dousl@hit.edu.cn(S.D); jpzhao@hit.edu.cn(J.Z); yaoli@hit.edu.cn(Y.L)

Abstract: A method for measuring the mechanical parameters of viscoelastic polymers by nanoindentation technology was proposed and verified. Through the mechanical response of load-displacement curves at different loading rates, then creep compliances and relaxation modulus were fitted. Polyimide thin film was employed in this research and experiments for five different loading rates were conducted. The fitting load-displacement loading curves obtained by the inversion method were identical to the experimental curves at five different loading rates，confirming the validity of the method. Moreover, with the loading rates increased，the fitting curves were more consistent commensurately with the nanoindentation experiment. DMA experiments were tested, and the generalized Kelvin/ Maxwell model were used for fitting experiment data. Results from DMA tests generally agree well with data from nanoindentation method, thereby verifying the feasibility of the method. The Prony series obtained by the two methods were used to simulate the creep experiments, which further verified the method.

Keywords: nanoindentation；viscoelasticity；creep compliance；relaxation modulus；Prony series

1. Introduction

With the increasing use of very small structures, nanocomposites and other micro-materials in various engineering areas such as optic, mechanical, electric and micro-electromechanical systems, a critical evaluation of the mechanic behavior is needed to predict the reliability of such materials [1-5]. Traditional mechanical testing is not suitable for small-scale or local performance testing due to the limitations of sample size, experimental conditions and test resolution [6-9]. Nanoindentation technology has become one of the most important methods for small-scale measurement because of its advantages of high resolution, simple sample preparation and non-destructive testing [10-14]. For general materials, nanoindentation technology can easily acquired hardness and elastic modulus, and more importantly, in the plastic region, the inversion calculation of constitutive relation can be carried out by dimensional analysis [15-17]. However, for time-dependent materials, the viscoelastic parameters cannot be directly measured, and the inversion calculation method proposed by previous researchers is not suitable, so how to obtain the mechanical properties of viscoelastic materials is one of the emphases. Unfortunately, there are few studies on calculation of viscoelastic parameters using nanoindentation.

Pal Jen Wei et al. [18] proposed the combination of one dashpot in series with one Kelvin model and two Kelvin models with distinct time constants in series to describe the deformation of polymers under indentation tests. A coupled experimental/numerical approach for the characterization of the local mechanical behavior of epoxy polymer materials was proposed by M. Minervino et al. They found that the pure viscoelastic constitutive law is not able to reproduce the local polymer behavior

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 July 2019 doi:10.20944/preprints201907.0243.v1

and needs be enhanced by adding material softening behavior [19]. Menčík J et al. [20] proposed a model consist of spring, plastic element, dashpot and two Kelvin–Voigt bodies to calculate the load response of viscoelastic-plastic materials, including biological and restorative biomaterials. In addition, some other models for viscoelastic polymers have been proposed as well [21-26]. Although efforts have been made to explain the viscoelastic properties of polymers, the models suggested in the previous studies are either very complex, resulting in time-consuming calculations or based on complex input data, such as complex loading profiles. On the other hand, the parameters obtained cannot be directly applied to engineering mechanical calculations, especially for simulation calculations.

The paper will propose and validate a method to directly calculate the viscoelastic parameters using nanoindentation test. The polyimide thin film (PI) was used to validate this method in this paper. The method can be acquiring creep compliance and relaxation modulus based on nanoindentation experiments at different loading rates. Comparatively, the DMA creep experiments were carried out, and then the viscoelastic parameter fitted by the generalized Kelvin/ Maxwell model, so that they can be used to compare with the results of nanoindentation method. Finally, Prony series calculated by the two methods are used in the creep simulation for verifying the method.

2. Theoretical background

The nanoindentation test can be regarded as a process in which a rigid indenter is gradually pressed into an elastic half-space. For a conical indenter, the relationship between load and displacement can be obtained by Sneddon contact model [27, 28].

$$P = \frac{4}{\pi(1-\upsilon)\tan\alpha} G h^2 \tag{1}$$

Similarly, according to this line of thought, when testing viscoelastic materials, the experimental process can be regarded as a quasi-static boundary issue between rigid indenter and semi-infinite space materials with time dependence. The difference between them is that viscoelastic materials have creep or relaxation characteristics due to their time dependence properties. Therefore, how to introduce time variable into contact model is a key factor. Load-displacement curve involves time factors such as loading rate, holding time, unloading rate, etc. In this paper, loading rate was used to express time variables.

According to Riande's research[29], the hereditary integral operator is introduced to equation (1) leads to the relationship between displacement and load：

$$h^2(t) = \frac{\pi(1-\nu)\tan\alpha}{4} \int_0^t J(t-\xi)[\frac{dp(\xi)}{d\xi}]d\xi \tag{2}$$

where $J(t)$ is the creep compliance.

The indentation load could be shows as $P(t) = v_0 t H(t)$ by the constant loading rate, where υ_0 being the loading rate and $H(t)$ the Heaviside unit step function. Let substitute $P(t)$ into equation(2)， we have

$$h^2(t) = \frac{\pi(1-\nu)v_0 \tan\alpha}{4} \int_0^t J(t-\xi)d\xi \tag{3}$$

Differentiating equation (3) with respect to t, we have

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 July 2019 doi:10.20944/preprints201907.0243.v1

$$J(t) = \frac{8h}{\pi(1-\nu)\tan\alpha}\frac{dh}{dp} \tag{4}$$

The general representation of the creep compliance based on the Kelvin model is

$$J(t) = J_0 + \sum_{i=1}^{N} J_i(1-e^{-t/\tau_i}) \tag{5}$$

where $J_0, J_1, J_2, \ldots J_n$ are compliance numbers, $\tau_1, \tau_2, \ldots \tau_n$ are retardation times, and N is a positive integer.

Substituting equation (5) into equation (4), we have

$$h^2(t) = \frac{1}{4}\pi(1-\nu)\tan\alpha[(J_0 + \sum_{i=1}^{N} J_i)P(t) - \sum_{i=1}^{N} J_i v_0 \tau_i (1-e^{-P(t)/(v_0\tau_i)})] \tag{6}$$

Equation (6) is the viscoelastic contact model based on nanoindentation technology. Apply the nanoindentation experiments at different loading rates, the relationship between loads and displacement squares can be obtained, and different creep parameters can be fitted soon. Therefore, the equation can analyze the viscoelastic relationship of time-dependent materials. According to the Laplace transformation, there is a conversion relationship between creep compliance and relaxation modulus in the Laplace domain, as shown in the equation (7), hence the relaxation modulus can be obtained by creep compliance [30].

$$E(t) = L^{-1}\{\tilde{E}(s)\} = L^{-1}(\frac{1}{s^2\tilde{J}(s)}) \tag{7}$$

where $E(t)$ is relaxation modulus, $L\{\}$ is Laplace operator.

3. Experiments

A commercial polyimide thin film was adopted in our study. The polyimide precursor reacted from the pyromelliticdianhydride (PMDA) and p,p'-oxy-dianline (ODA). Specimen surface was cleaned and all specimens were aged for approximately 48 hours before nanoindentation tests. All nanoindentation tests were performed at room temperature. Nanoindentation experiments were carried out in a stress loading manner, and the constant loading is 10 mN. Five fixed loading rates of 2 mN/s, 1 mN/s, 0.5 mN/s, 0.1 mN/s and 0.05 mN/s were tested, respectively. For each sample, at least five tests were conducted to calculate the average value of the mechanical parameters.

Similarly, after the surface cleaning, samples were prepared by the mechanical cutting for DMA creep tests. The creep tests of PI film were performed with film tension mode using DMA Q800 (TA Instruments, DE, USA) dynamic mechanical analyzer. The DMA tests were performed under controlled stress. In order to improve the accuracy of the tests, a preliminary test was carried out at room temperature with the constant stress equal to 0.1MPa. Immediately after the preliminary test, the samples were keeping 30 min at the test temperature. The initial stress was 5MPa.Therefore when the stress reached the setting point, the value of strain with time change was recorded, and then the creep curves were obtained.

4. Results and discussion

The experimental curves of nanoindentation are shown in Fig. 1. It is obvious that when the maximum loads in the same value, different loading rates show the same trend of variation, however, show the different maximum displacements. This indicates that polyimide film has time dependence, so when the time for reaching the maximum load is different, causing different curve values.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 July 2019 doi:10.20944/preprints201907.0243.v1

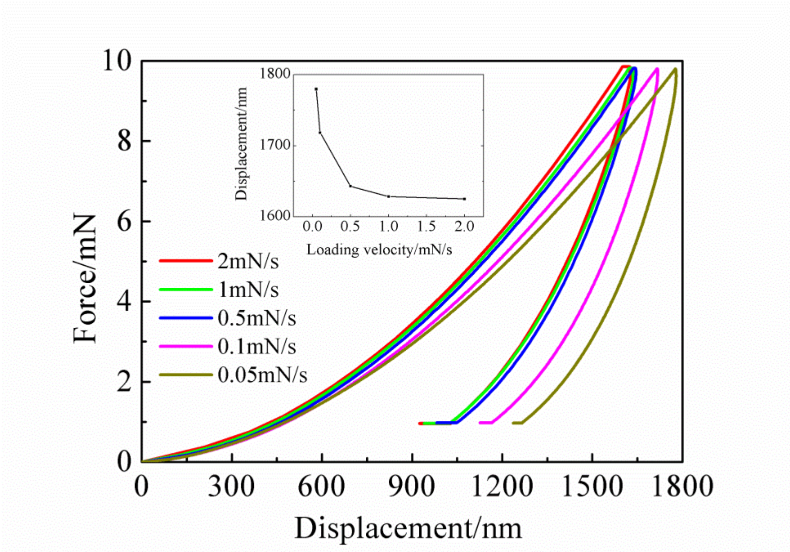

Figure 1. The load-displacement curves for PI materials by nanoindentation under different loading rates.

It is noteworthy that when the loading rate is larger, the load-displacement curves obtained by the experiment basically coincide with each other. With the decrease of loading rate, the discrete phenomenon of load-displacement curve begins to appear. The slower the loading rate, the more obvious the discrete phenomenon of displacement curves. This is because the polyimide thin film is viscoelastic material, which is time-dependent. When the loading rate is slower, thus the loading time is longer. Therefore, creep phenomenon occurs during the loading process, which is consistent with the research in other literature [31-33].

According to the nanoindentation test data and the equation (5), the relationship between $h^2(t)$ and $P(t)$ under different loading rates can be obtained, the creep compliance can be can be analyzed.

Owing to the angle between the indenter and the measured material plane is $19.7°$, the equation (6) can be simplified as follows

$$h^2(t) = 0.1883[(J_0 + \sum_{i=1}^{N} J_i)P(t) - \sum_{i=1}^{N} J_i v_0 \tau_i (1 - e^{-P(t)/(v_0 \tau_i)})] \tag{8}$$

The data of load-displacement curves at five loading rates are introduced and we get

when the loading rate is 2 mN/s,

$$\begin{aligned} h^2(t) = 0.1883[&0.0012953P(t) - 0.00319(1 - e^{-P(t)/18.46}) - 0.0054(1 - e^{-P(t)/172.42}) \\ &- 0.3068(1 - e^{-P(t)/2000})] \end{aligned} \tag{9}$$

when the loading rate is 1 mN/s,

$$\begin{aligned} h^2(t) = 0.1883[&0.0012953P(t) - 0.001596(1 - e^{-P(t)/9.32}) - 0.0027(1 - e^{-P(t)/86.21}) \\ &- 0.1534(1 - e^{-P(t)/1000})] \end{aligned} \tag{10}$$

when the loading rate is 0.5 mN/s,

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 July 2019 doi:10.20944/preprints201907.0243.v1

$$h^2(t) = 0.1883[0.0012953P(t) - 0.000798(1 - e^{-P(t)/4.66}) - 0.00135(1 - e^{-P(t)/43.105}) - 0.0766(1 - e^{-P(t)/500})] \tag{11}$$

when the loading rate is 0.1 mN/s,.

$$h^2(t) = 0.1883[0.0012953P(t) - 0.0001596(1 - e^{-P(t)/0.932}) - 0.00027(1 - e^{-P(t)/8.621}) - 0.01532(1 - e^{-P(t)/100})] \tag{12}$$

when the loading rate is 0.05 mN/s,

$$h^2(t) = 0.1883[0.0012953P(t) - 0.0000798(1 - e^{-P(t)/0.466}) - 0.000135(1 - e^{-P(t)/4.315}) - 0.00766(1 - e^{-P(t)/50})] \tag{13}$$

The fitted loading curve can be inversed by the equations (9)-(13), and then compared with the loading curve of nanoindentation experiment, as shown in Fig. 2. It can be seen that the loading curve under five different loading rates calculated by viscoelastic contact model of nanoindentation is consistent with the nanoindentation experiment, and the value dispersion is smaller, especially in the case of shallow indentation depth. It can also be seen that with the increase of the loading depth, the fitting curve and the experimental curve have certain discrete deviation. However, the overall fitting degree is good, which verifies the validity of the function based on nanoindentation technology. It can be seen that with the increase of loading rate, the position of discrete points in the loading curve is larger, which fully demonstrates the viscoelastic behavior of polyimide film. At the same time, it also shows that the function proposed in this paper is applicable to the shallow loading depth experiments, and with the increase of indentation depth, the error gradually appears.

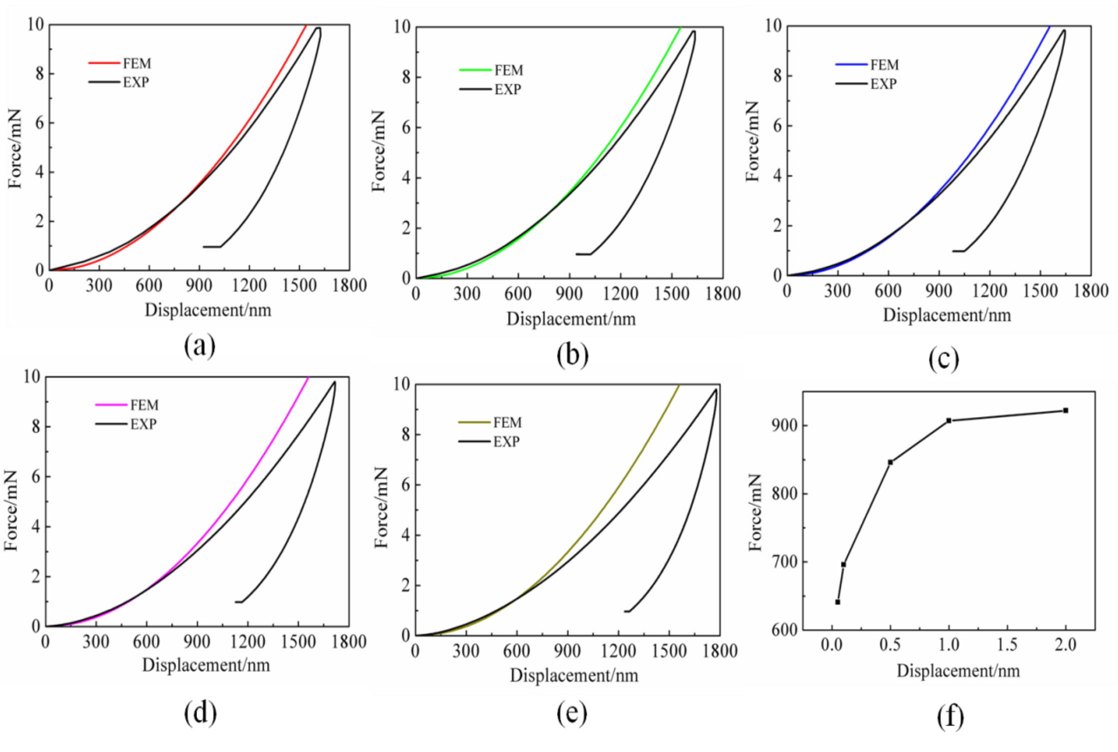

Figure 2. Fitting curves and discrete points at different loading rates. (a)2mN/s, (b)1mN/s ,(c)0.5mN/s, (d)0.1mN/s ,(e)0.05mN/s, (f) discrete points at different loading rates

According to equations (9)-(13), creep compliance of polyimide film can be deduced

$$J(t) = 0.0009397 + 0.0001712(1-e^{-t/9.23}) + 0.00003104(1-e^{-t/86.21}) + 0.0001534(1-e^{-t/1000}) \quad (14)$$

Fig.3 is the creep compliance curves comparison obtained between the inversion of viscoelastic contact model based on nanoindentation technology and DMA creep experiments. It can be concluded that the two curves have the same development trend，less discrete in creep compliance values and in good fitting degree with the increase of time. These proved that the viscoelastic contact model based on nanoindentation technology is reasonable, and the creep compliance calculation method based on nanoindentation experiment is feasible.

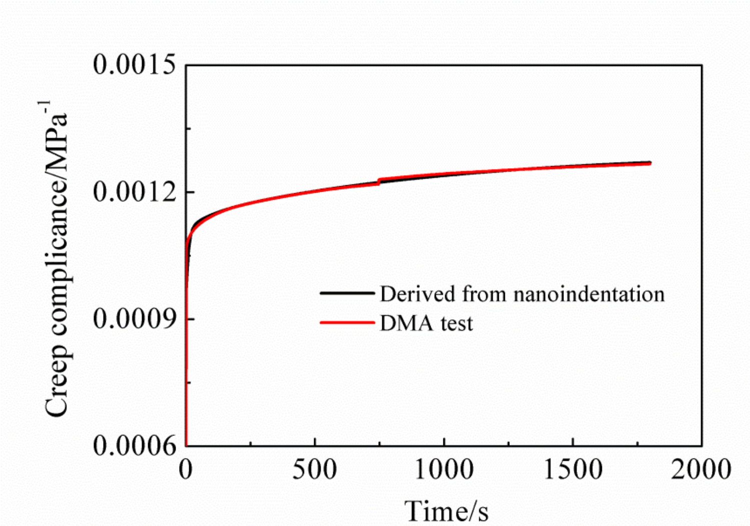

Figure 3. Creep compliance comparisons between derived from nanoindentation experiment and DMA test.

According to the equation (7), the calculated creep compliance can be converted into relaxation modulus, and it can be concluded that:

$$E(t) = 775 + 104.4e^{-t/20} + 40.85e^{-t/200} + 76.44e^{-t/1200} \quad (15)$$

Similarly，the creep compliance calculated by DMA experiment can transformed for relaxation modulus. By introducing the parameters into the 3-element generalized Maxwell model (Supporting Information), the equation can be obtained:

$$E(t) = 771.4 + 45.93e^{-t/20} + 45.58e^{-t/300} + 76.67e^{-t/1200} \quad (16)$$

Fig.4 is the comparison of relaxation modulus between the transformed of DMA creep experiment, fitted by 3-element Maxwell model and calculated by viscoelastic contact model based on nanoindentation. It can be concluded that the three types of data have good fitting degree, which indicates that the results from the viscoelastic contact model is consistent with those from the traditional viscoelastic model, and verified the method.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 July 2019 doi:10.20944/preprints201907.0243.v1

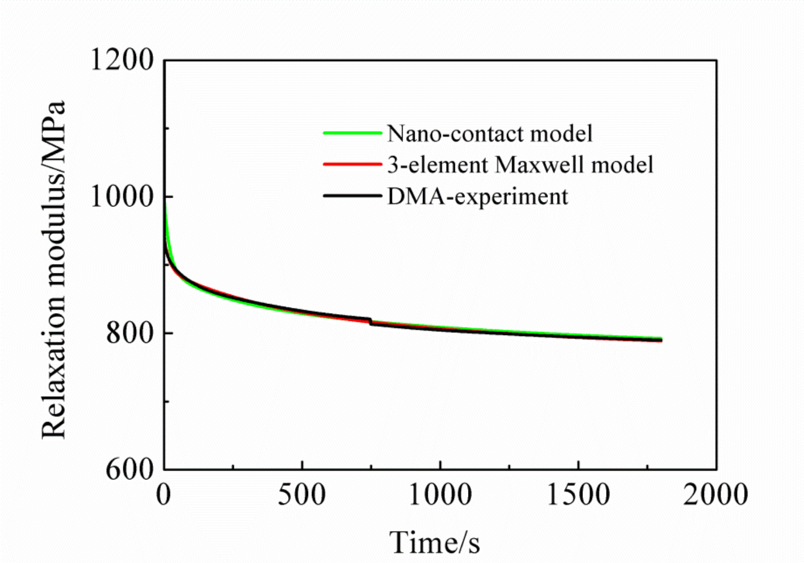

Figure 4. The curves of relaxation modulus by the method of 3-element Maxwell model, viscoelastic contact model based on nanoindentation and transformed of DMA creep experiment.

To be concluded, the viscoelastic model based on nanoindentation technology can calculate both the relaxation modulus and creep compliance. The calculated results are basically consistent with the traditional experiments, so it provided a new method to acquire viscoelastic properties.

5. FEM simulation

In order to further verify the viscoelastic parameters obtained by nanoindentation, the FEM is used to simulate creep test. The same size as the DMA test sample is selected to establish the geometric model, as shown in Fig.5. In this model, three-dimensional C3D8R element and hexahedral mesh are used. One end of the finite element geometric model is fully constrained and the opposite side is imposed with initial stress without constraint for other aspects.

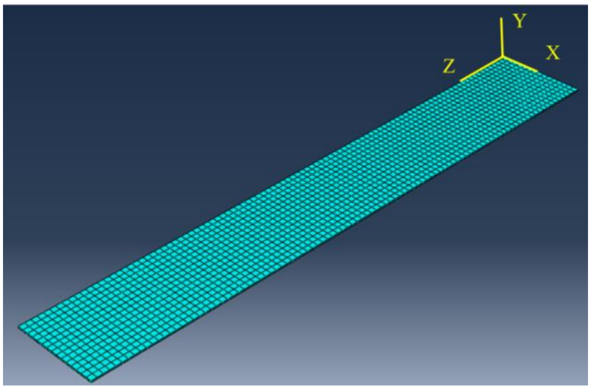

Figure 5. The simulation geometric model of PI thin film.

The simulation is carried out in two steps. The first step is quasi-static loading with the purpose to exert the initial stress; the second step is viscous loading, keeping the initial stress for 30 min, and observing the occurrence of creep phenomena in this time range. The parameters input to the model are Prony series converted by the creep compliance, as shown in Table 1.

Table 1. Prony series under two methods.

Prony series	DMA test	Nanoindentation
G_1=K_1	0.0489	0.1047

$G_2=K_2$	0.0485	0.0410
$G_3=K_3$	0.0816	0.0767

Fig.6 is the comparison of the creep results between the input two types of Prony series and experiment. It can be seen that the simulation curves obtained by the two methods are well consistent with the experimental curves of DMA. The experimental data curves are slightly lower than the simulated data curves, but the overall error is small, which verifies the accuracy of the method. It is proved that the viscoelastic model based on nanoindentation can be applied to polyimide materials, and it also provides a calculation method for other viscoelastic polymers.

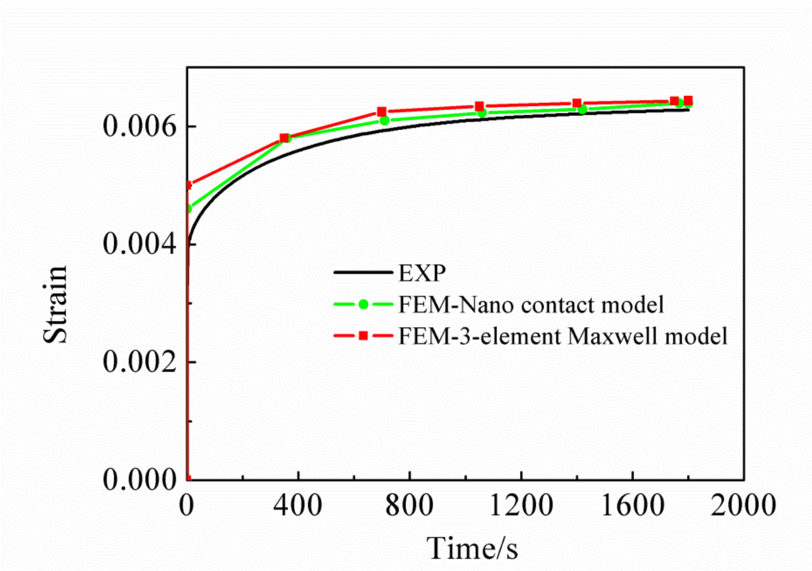

Figure 6. The comparison of simulation results under three types of viscoelastic parameter.

6. Conclution

A contact model for measuring viscoelastic parameters based on nanoindentation was proposed and validated. The viscoelastic mechanical response of load-displacement curve was achieved by nanoindentation experiments at different loading rates. The fitted viscoelastic parameters of the polyimide film were identical to the values fitted by traditional DMA experiments, confirming the rationality of the method. The fitting loading curves at five different rates were obtained by the inversion method, which were nearly the same as the loading curves of nanoindentation experiments. Moreover, the fitting curves were more consistent with the bigger loading rates. Based on the Prony series of the generalized Kelvin model, the finite element numerical simulation was conducted, further confirming the feasibility of this method and providing a new idea for viscoelastic polymer materials which in small scale.

Reference

[1] Díez-Pascual A M, Gómez-Fatou M A, Ania F, et al. Nanoindentation in polymer nanocomposites[J]. Progress in Materials Science, 2015, 67: 1-94.

[2] Gibson R F. A review of recent research on nanoindentation of polymer composites and their constituents [J]. Composites Science and Technology, 2014, 105: 51-65.

[3] Voyiadjis G Z, Malekmotiei L, Samadi-Dooki A. Indentation size effect in amorphous polymers based on shear transformation mediated plasticity [J]. Polymer, 2018, 137: 72-81.

[4] Yoo B G, Choi I C, Kim Y J, et al. Room-temperature anelasticity and viscoplasticity of Cu–Zr bulk metallic glasses evaluated using nanoindentation[J]. Materials Science and Engineering: A, 2013, 577: 101-104.

[5] Voyiadjis G Z, Malekmotiei L. Variation of the strain rate during CSM nanoindentation of glassy polymers

and its implication on indentation size effect [J]. Journal of Polymer Science Part B: Polymer Physics, 2016, 54(21): 2179-2187.

[6] He W, Goudeau P, Le Bourhis E, et al. Study on Young's modulus of thin films on Kapton by microtensile testing combined with dual DIC system [J]. Surface and Coatings Technology, 2016, 308: 273-279.

[7] Giró-Paloma J, Roa J J, Díez-Pascual A M, et al. Depth-sensing indentation applied to polymers: A comparison between standard methods of analysis in relation to the nature of the materials[J]. European Polymer Journal, 2013, 49(12): 4047-4053.

[8] Martinez R, Xu L R. Comparison of the Young's moduli of polymers measured from nanoindentation and bending experiments [J]. MRS Communications, 2014, 4(3): 89-93.

[9] Tvergaard V, Needleman A. Polymer indentation: numerical analysis and comparison with a spherical cavity model [J]. Journal of the Mechanics and Physics of Solids, 2011, 59(9): 1669-1684.

[10] Jin C, Ebenstein D M. Nanoindentation of compliant materials using Berkovich tips and flat tips [J]. Journal of materials research, 2017, 32(2): 435-450.

[11] Yang Y. Sensitivity of nanoindentation strain rate in poly (ester-ester-ketone) using atomic force microscopy [J]. Polymer Testing, 2016, 53: 85-88.

[12] Jin T, Niu X, Xiao G, et al. Effects of experimental variables on PMMA nano-indentation measurements [J]. Polymer Testing, 2015, 41: 1-6.

[13] Feng G, Ngan A H W. Effects of creep and thermal drift on modulus measurement using depth-sensing indentation [J]. Journal of materials research, 2002, 17(3): 660-668.

[14] Frontini P, Lotfian S, Monclús M A, et al. High temperature nanoindentation response of RTM6 epoxy resin at different strain rates [J]. Experimental Mechanics, 2015, 55(5): 851-862.

[15] Oliver W C, Pharr G M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments [J]. Journal of materials research, 1992, 7(6): 1564-1583.

[16] Chollacoop N, Dao M, Suresh S. Depth-sensing instrumented indentation with dual sharp indenters [J]. Acta materialia, 2003, 51(13): 3713-3729.

[17] Dao M, Chollacoop N, Van Vliet K J, et al. Computational modeling of the forward and reverse problems in instrumented sharp indentation [J]. Acta materialia, 2001, 49(19): 3899-3918.

[18] Wei P J, Shen W X, Lin J F. Analysis and modeling for time-dependent behavior of polymers exhibited in nanoindentation tests[J]. Journal of Non-Crystalline Solids, 2008, 354(33): 3911-3918.

[19] Minervino M, Gigliotti M, Lafarie-Frenot M C, et al. A coupled experimental/numerical approach for the modelling of the local mechanical behaviour of epoxy polymer materials [J]. Journal of the Mechanics and Physics of Solids, 2014, 67: 129-151.

[20] Menčík J, He L H, Swain M V. Determination of viscoelastic–plastic material parameters of biomaterials by instrumented indentation [J]. Journal of the mechanical behavior of biomedical materials, 2009, 2(4): 318-325.

[21] Seltzer R, Mai Y W. Depth sensing indentation of linear viscoelastic–plastic solids: a simple method to determine creep compliance [J]. Engineering Fracture Mechanics, 2008, 75(17): 4852-4862.

[22] Song R, Muliana A H, Palazotto A. An empirical approach to evaluate creep responses in polymers and polymeric composites and determination of design stresses [J]. Composite Structures, 2016, 148: 207-223.

[23] Zhai M, McKenna G B. Viscoelastic modeling of nanoindentation experiments: A multicurve method [J]. Journal of Polymer Science Part B: Polymer Physics, 2014, 52(9): 633-639.

[24] Herbert E G, Phani P S, Johanns K E. Nanoindentation of viscoelastic solids: A critical assessment of experimental methods [J]. Current opinion in solid state and materials science, 2015, 19(6): 334-339.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 July 2019 doi:10.20944/preprints201907.0243.v1

[25] Oliveira G L, Costa C A, Teixeira S C S, et al. The use of nano-and micro-instrumented indentation tests to evaluate viscoelastic behavior of poly (vinylidene fluoride)(PVDF)[J]. Polymer Testing, 2014, 34: 10-16.
[26] Xia W, Song J, Hsu D D, et al. Understanding the interfacial mechanical response of nanoscale polymer thin films via nanoindentation[J]. Macromolecules, 2016, 49(10): 3810-3817.
[27] Sneddon I N. The relation between load and penetration in the axisymmetric Boussinesq problem for a punch of arbitrary profile [J]. International journal of engineering science, 1965, 3(1): 47-57.
[28] Cheng Y T, Cheng C M. General relationship between contact stiffness, contact depth, and mechanical properties for indentation in linear viscoelastic solids using axisymmetric indenters of arbitrary profiles [J]. Applied Physics Letters, 2005, 87(11): 111914.
[29] Riande E, Diaz-Calleja R, Prolongo M, et al. Polymer viscoelasticity: stress and strain in practice[M]. CRC Press, 1999.
[30] Hernandez-Jimenez A, Hernandez-Santiago J, Macias-Garcıa A, et al. Relaxation modulus in PMMA and PTFE fitting by fractional Maxwell model [J]. Polymer Testing, 2002, 21(3): 325-331.
[31] Lee Y J, Huang J M, Kuo S W, et al. Low-dielectric, nanoporous polyimide films prepared from PEO–POSS nanoparticles[J]. Polymer, 2005, 46(23): 10056-10065.
[32] Crochon T, Li C, Lévesque M. On time–temperature-dependent viscoelastic behavior of an amorphous polyimide [J]. Mechanics of Time-Dependent Materials, 2015, 19(3): 305-324.
[33] Xia R, Zhou H, Wu R, et al. Nanoindentation investigation of temperature effects on the mechanical properties of nafion® 117[J]. Polymers, 2016, 8(9): 344.