INDENTATION CREEP OF POLYMERIC MATERIALS: EXPERIMENTAL AND ANALYSIS

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ABSTRACT

This paper presents studies on time-dependent properties, namely creep behavior, of polymeric materials by indentation techniques. A semi-empirical model in which includes the elastic-viscoelastic-viscous properties (EVEV model) by using a generalized Kelvin model to analyze indentation creep has been established. It is shown that this EVEV model can fit well the experimental creep data and to give the exact changes of creep behavior during nanoindentation. The creep deformations of different polymeric materials, including amorphous thermoplastic, thermosetting and polymer-clay nanocomposites have been studied in details. It has also proposed a method to determine the elastic modulus and viscosity coefficient in which is independent of the holding and unloading process of the indentations, again, the elastic modulus derived based on this new analysis has good agreement with that from other methods. The creep deformation is further used to derive creep compliance and retardation spectrum, which are very useful to predict other mechanical properties of polymeric materials. The indentation creep behavior of polymers have been also associated with their molecular structures, such as molecular weight, and cross-linking density. This model and analysis is useful to understand the mechanical properties of the polymeric materials.

Theoretical analysis by using generalized viscoelastic models has been also performed to verify the EVEV model proposed in this study. The viscoelastic properties of several polymers are extracted by fitting the experimental results based on this theoretical analysis and compared with that from the EVEV model. The creep constitutive models for thermoplastic and thermosetting polymers are suggested. A good agreement is obtained between the experiments and theoretical model.

The experimental and theoretical works together provide a new scheme for analyzing and application of the indentation creep experiments. This experiments and analysis are further extended to the indentation creep experiments at elevated temperature for thermoplastic and thermosetting polymers, and the results again show good agreement between the experiments and theoretical analysis.

1 INTRODUCTION

In this paper, we will present studies of polymer creep by using nanoindentation with flat-ended punch and sharp Berkovich tip (MTS Nan-indenter XP) for numbers of amorphous polymers and polymer based composites. A recent developed elastic-viscoelastic-viscous (EVEV) model [1] is used to fit and analyze the indentation creep of polymeric materials including PMMAs, Epoxies, and epoxy-clay nanocomposites. The EVEV model is derived based on a generalized Kelvin model, which can be used to describe the indentation creep behavior of polymers. Further, this model is used to derive an empirical formula to fit the experimental creep data. Using this model, the elastic modulus and viscosity coefficient can be calculated by applying the parameters in the creep formula and avoiding the use of the unloading data; therefore, the derived elastic modulus is independent of the holding time and unloading rate. Furthermore, the creep formula is used to derive the creep compliance and retardation spectrum of the polymeric materials from the nanoindentation experiments. This information is very useful when we discuss the influence of molecular structure on the indentation creep experiments.

2 EVEV MODEL

We are using a generalized Kelvin model as shown in Fig. 1 to model the indentation creep behavior. The EVEV model includes a series of parallel-linked dashpots and linear springs (Kelvin units) plus one linear spring and one dashpot. It has been shown that at least three Kelvin units are needed to model the creep behavior during indentation [1]. Based on the elastic solution of the flat-ended punch indentation together with stress analysis of the indentation creep experiments, the creep deformation during indentation can be expressed as:

$$h = h_{in}\frac{P_0}{E_0 A_0} + \sum_i^n \frac{P_0 h_{in}}{E_i A_0}\left(1 - e^{-E_i t/\eta_i}\right) + \frac{h_{in}}{\eta_0}t = h_e + \sum_i^n h_i\left(1 - e^{-t/\tau_i}\right) + t/\mu_0 \qquad (1)$$

where h is the indentation creep displacement; h_{in} is a virtual length which is used to define the indentation strain as $\varepsilon = h/h_{in}$, and its value is equal to the elastic-plastic displacement (*i.e.*, the total indentation displacement); P_0 is the constant indentation load for the indentation creep experiments; E_0 is the elastic

modulus of the materials; A_0 is the initial contact area at the beginning of the indentation creep experiment and can be determined by using the calibrated indenter area function; E_i and η_i are the elastic modulus and viscosity coefficient for the *ith* Kelvin unit in the EVEV model, respectively; η_0 is the viscosity coefficient of the polymer, and t is the creep time, and n is the numbers of the Kelvin units, and the value $n=3$ based on previous study is sufficient to model the indentation creep experiments. It has been approved that eqn.(1) can be used equally well for the case of sharp indenter tip, such as Berkovich tip [1].

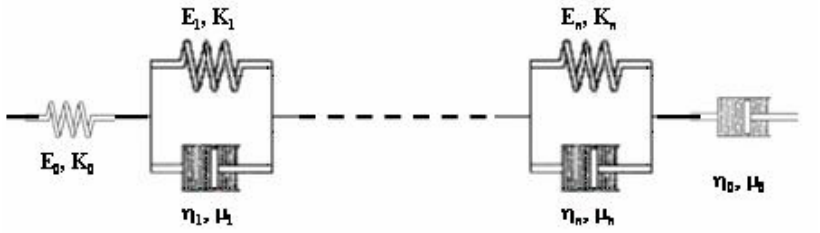

Figure 1, A generalized viscoelastic model was used in the analysis of nanoindentation creep

Eqn.(1) demonstrates that an indentation creep should include three contributions to the deformation: instantaneous displacement, h_e, resulting from the elastic deformation of the materials during loading, the viscoelastic deformation controlled by the exponential terms in eqn (1), and viscous deformation during creep. The instantaneous displacement, h_e, can be used to determine the elastic modulus as:

$$E_0 = P_0 h_{in} / A_0 h_e \tag{2}$$

and the viscous term in eqn (1) can be used to determine the viscocity coefficient of the materials as:

$$\eta_0 = h_{in} \mu_0 \tag{3}$$

The instantaneous displacement, h_e, can be determined by using Oliver and Pharr's unloading analysis [2], using part of the unloading data.

3 MATERIALS AND INDENTATION EXPERIMENTS

The materials used in this study included four Poly(methymethacrylate) (PMMA) samples with different molecular weight, four epoxy samples with different cross-linking density and Epoxy- 5% clay (wt%) nanocomposites. In this study, PMMA represents amorphous thermoplastic polymer, and epoxy is the cross-linked thermosetting polymer.

Indentation creep experiments were performed by using a Nanoindenter XP (MTS, TN, USA) with a flat-ended punch tip and standard Berkovich indenter tip. The tests were done under load-control with a constant loading rate. The flat-ended punch tip experiments were used to fit the theoretical analysis, whereas the sharp indentation experiments were used to fit the EVEV model. The indentation procedure has been described in details before [1], and was shown schematically in Fig. 2. The key factors in this procedure were fast loading rate and the two-steps unloading. The fast loading and unloading segments were designed to minimize the influences viscoelastic properties of the polymer on the indentation data. The first unloading segment was used to determine the elastic deformation, whereas the reduced rate unloading (second unloading segment) was designed to avoid recording negative load values for the recovery test due to the fast unloading rate. However, there were always overshot loads due to the fast loading, therefore the indentation creep experiments were done at somewhat different holding load, although at least 10 indents were done at the same conditions, but the holding loads for the creep experiments were different, therefore, no average could be done in such case.

4 RESULTS AND DISCUSSION

The indentation creep results and the curve fitting from eqn. (1) for different molecular weight PMMAs are shown in Fig.3, the same results for epoxies with different cross-linking densities are showed in Fig.4, and Fig. 5 for the same results for Epoxy-clay nano-composite.

For PMMAs, the results show that the creep becomes more remarkable with the decreases of the molecular weight (Fig.3). However, the creep rates at different stages of the creep are very different. The creep rate is faster for higher molecular weight PMMAs than that of the lower molecular weight at the beginning of the creep, and the creep rate becomes slower for the higher molecular weight PMMAs than

that of the lower molecular weight after certain time. The creep is more sensitive for PMMAs with high molecular weight at the start of the creep tests, which can be reflected from the slope of the creep deformation curve and also the retardation time.

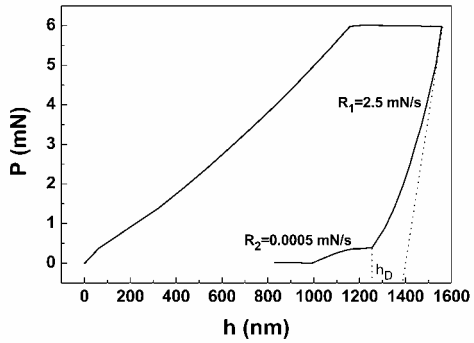

Figure 2, Schematic diagram showing the nano-indentation procedure: two-steps unloading are used during the indentation creep.

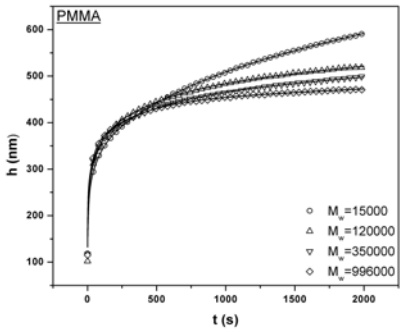

Figure 3, Creep deformation and fitting curves based on eqn.(1) for PMMAs with different molecular weight.

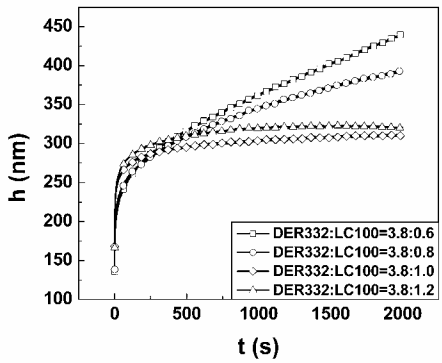

Figure 4, Creep deformation and fitting curves based on eqn.(1) for epoxies with different cross-linking densities

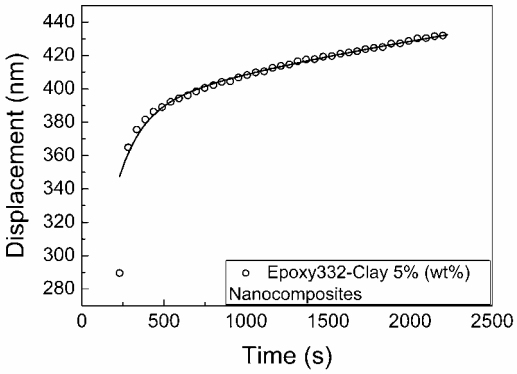

Figure 5, Creep deformation and fitting curves based on eqn (1) for epoxy with 5% clay nanocomposite

For epoxies, the results show that the cross-linking density affects the epoxy creep rates significantly, especially for the samples with low cross-linking density (Fig. 4). When the crosslinking density increases, the creep deformation decreases dramatically as the amount of the curing agent increases. The increases of the amount of curing agent increases the cross-linking density until the ratio between the epoxy resin and curing agent reaches to their stoichiometric ratio.

For epoxy-clay composite, we found that this EVEV model did not capture well the initial change of the creep deformation as the case of pure epoxy (Fig.5). Comparing with the results of epoxy, the retardation time of the nanocomposite shows large different from that of the epoxy, indicating the additional of clay has changed the deformation mechanisms of polymer nanocomposites.

5 THEORETICAL ANALYSIS

The theoretical analysis was based on the case of flat-ended punch indentation. Laplace transformations were used to derive the viscoelastic model to describe the creep deformation of the polymers during indentation by flat ended punch tip [3]. Three viscoelastic deformation models, in which were corresponded to different combination of the generalized Kelvin model, were derived. Model (a) was one spring, one Kelvin unit and one dashpot connected in series; model (b) was one spring and two Kelvin units connected in series, this model did not have separated dashpot as that in the Model (a), and model (c)

was one spring, two Kelvin units and one dashpot connected in series. The viscoelastic solution for the indentation creep can be expressed as following:

$$h = h_0 + \mu_0 t - \sum_i^3 h_i e^{-t/t_i} \qquad \textit{model (a)} \tag{4a}$$

$$h = h_0 - \sum_i^4 h_i e^{-t/t_i} \qquad \textit{model (b)} \tag{4b}$$

$$h = h_0 + \mu_0 t - \sum_i^5 h_i e^{-t/t_i} \qquad \textit{model (c)} \tag{4c}$$

where h_0, h_i and t_i are fitting constants related to the elastic constant (E_0 and E_i) of the springs and the viscocity coefficient (η_0 and η_i) of the dashpots respectively. By applying Genetic Algorithm optimizing method, eqn (4) can be used to fit the indentation creep experiments by using flat-ended punch tip. The results are shown in Fig. 6(a) for PMMA and Fig. 6(b) for epoxy. These theoretical analyses showed that to model the long-time creep behavior of the polymeric materials, at least two Kelvin units are needed as shown in Model (c). If one only needs to extract the elastic modulus, simple models as such Model (a) is accurate enough, since the elastic modulus in such case only related to the instantaneous deformation during indentation. The viscoelastic deformation is more complicated, and one would need at least two Kelvin units in the material constitutive relations, so that a wider time scale can be covered. Most of polymeric materials, especially thermoplastic polymers show large irreversible deformation during indentation, therefore a separate dashpot is needed for most of those analysis.

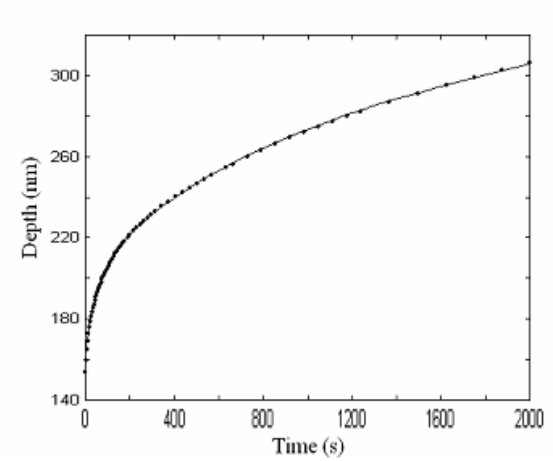

Figure 6 (a), Comparison of fitting curves based on model (c) and experimental data of PMMA.

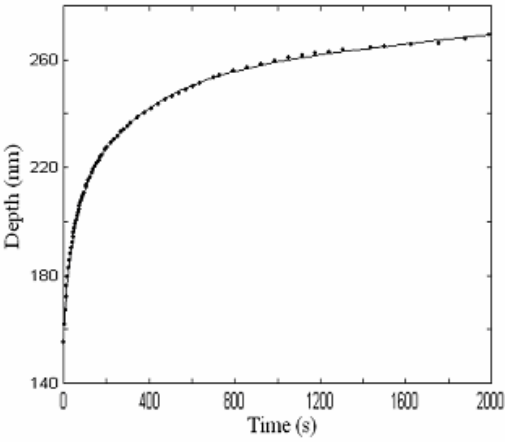

Figure 6 (b), Comparison of fitting curves based on model (c) and experimental data of Epoxy

The EVEV model and the theoretical analysis agreed well with the molecular theory of viscoelasticity [4]. There are three major types of mechanisms associated with the deformation of polymeric materials. The first type is the bending and stretching of inter- and intra-molecular bonds, which gives rise to an instantaneous elastic deformation. This type of deformation can be well described by the deformation of spring. The second type is time-dependent elastic deformation, which does not involve irreversible chain deformation, and therefore can be fully recovered. This type of deformation is usually described by the Kelvin unit with one spring and one dashpot. However, this type of deformation can occur at different length scales, therefore, several characteristic times may exist. Therefore several such units may be needed to describe this feature. The last is the irreversible deformation, corresponding to the dashpot. This study shows that indentation creep experiments covered several characteristic times and therefore the generalized model is needed to describe the indentation creep experiments.

6 MICRO-INDENTATION CREEP AT ELEVATED TEMPERATURE

We further carried the indentation creep experiments at several elevated temperatures by using micro-indentation experiments with sharp Berkovich indenter tips. The materials being tested are PC and epoxy. The temperatures were selected from room temperature to more than 50% of T_g of the testing materials. The results are presented in Fig.7. It shows clearly that the EVEV model can be well applied to the different loads and temperature range and shows good agreement with the experimental results.

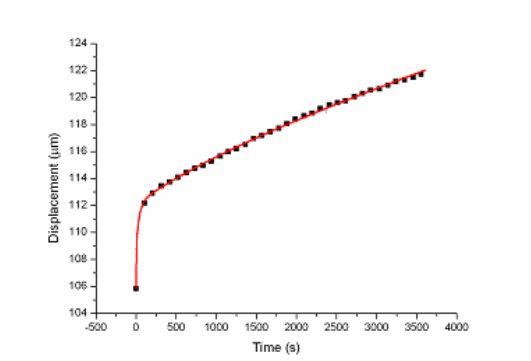

Figure 7 (a,) Microindentation creep data and curve fitting of EVEV model for polycarbonate at 100°C, 10 N load and 3600s creep time.

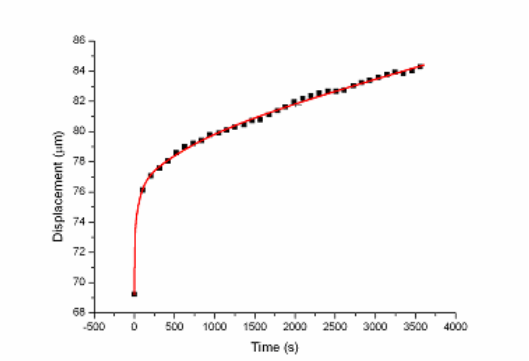

Figure 7 (b), Microindentation creep data and curve fitting of EVEV model for epoxy at 150°C 10 N load and 3600s creeping time.

7 CREEP COMPLIANCE AND RETARDATION SPECTRUMS

The significance of polymer creep equation is due to its association with other mechanical properties of materials. In general, the creep compliance and retardation spectrum can be derived from the creep data. Similar to the tensile creep testing, the indentation creep compliance can be written as:

$$J(t)=\frac{A_0}{P_0 h_{in}}h(t)=J_e+\sum_1^3 J_i\left(1-e^{-t/\tau i}\right)+t/\eta_0 \qquad (5)$$

and the retardation spectrum can be derived as [5]:

$$L(\tau)=\sum_1^3\left[\left(1+\frac{t}{\tau_i}\right)\frac{h_i}{\tau_i}e^{-t/\tau i}\right]\frac{A_0}{P_0 h_{in}}t\Big|_{t=2\tau} \qquad (6)$$

where $J(t)$ is the creep compliance and $L(\tau)$ is the retardation spectrum. The creep compliance and retardation spectrum usually shows clearly the effects of molecular structures on the indentation creep characteristics. The creep compliance curve for PMMAs are shown in Fig. 8 and the retardation spectrum is

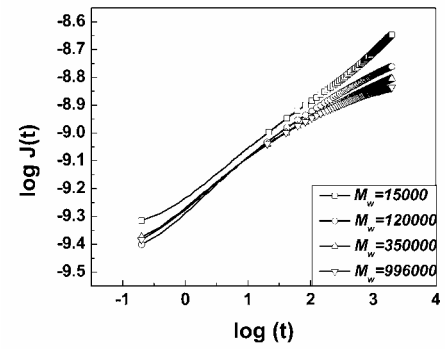

Figure 8, Creep Compliance of PMMAs in the double-logrithmic plot.

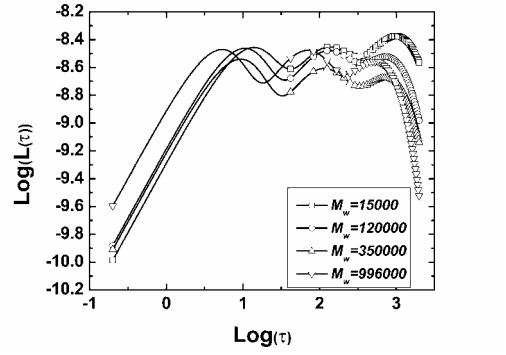

Figure 9. Retardation spectrum of PMMAs in the double-logrithmic plot.

shown in Fig. 9 as examples. The creep compliance at long creep time appears to approach a limited value, indicating that that the viscous flow contributions are limited as the creeping time increases. The limited value of creep compliance is usually related to the energy stored in all the springs in the EVEV model during a steady-state flow. It measures the average distortion of the polymer chain during flow. The PMMAs with higher molecular weight show more clearly the limited value of the creep compliance, indicating the viscous flow is difficult as the molecular weight increases.

For the retardation spectrum, the slope of the region prior to the first retardation peak is usually corresponding to the short-time region and represents local motions of the polymer chain, or non-polymeric modes. The peaks at the retardation spectrum are usually considered to be due to polymeric modes. The peak separation is usually used to measure the rubbery plateau.

8 ELASTIC MODULUS AND VISCOCITY COEFFICIENT

The elastic modulus is determined from the instantaneous deformation during loading, the values determined from this analysis agreed well with those reported in the literature as well as measured by other mechanical testing methods include DMA testing. This method has the advantage that the elastic modulus is independent of holding time if the steady-state creep can be reached.

The viscosity coefficient is another important parameter in which can be determined from this study. It has been shown that it has been affected significantly by the molecular structures such as molecular weight or cross-linking density. Higher viscosity coefficient indicates less viscous flow during the creep experiments. For PMMA, the increases of molecular weight increases the viscosity coefficient indicating less viscous flow when the molecular weight increase. For epoxy, as the cross-linking density increases, the viscosity coefficient also increases, again, indicating the decreased viscous flow as the increasing of cross-linking density.

9 SUMMARY AND CONCLUSIONS

In this paper, we first present a semi-empirical EVEV model to characterize the indentation creep properties of numbers of polymeric materials. Then a further theoretical analysis provides a theoretical foundation for the mathematical form of the EVEV model. Both EVEV model and theoretical analysis show good agreement with the indentation creep experiments. Further, a method to extract elastic modulus and viscosity coefficient has been also proposed. Finally, the indentation creep experimental and the EVEV model can also be well extended to high load and high temperature to characterize the creep behavior of polymeric materials.

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