한국소성가공학회 2009년도 춘계학술대회 논문집 pp. 70~73

열방식 마이크로 임프린트 공정을 위한 고분자 재료의 수치적 모델링

란 슈하이[1]· 이혜진[2]· 이형욱[3]· 송정한[2]· 이수훈[4]· 준 니[5]· 이문구[4#]

Experimental and Numerical Study on the Viscoelastic Property of Polycarbonate near Glass Transition Temperature for Micro Thermal Imprint Process

Shuhuai Lan[1], Hey-Jin Lee[2], Hyoung-Wook Lee[3], Jung-Han Song[2], Soo-Hun Lee[4], Jun Ni[5], Moon G. Lee[4#]

Abstract

The aim of this research is to obtain a numerical material model for an amorphous glassy polymer, polycarbonate (PC), which can be used in finite element analysis (FEA) of the micro thermal imprint process near the glass transition temperature. An understanding of the deformation behavior of the PC specimens was acquired by performing tensile stress relaxation tests. The viscoelastic material model based on generalized Maxwell model was introduced for the material near Tg to establish the FE model based on the commercial FEA code ABAQUS/Standard with a suitable set of parameters obtained for this material model from the test data. Further validation ofthe model and parameters was performed by comparing the analysis of FE model results to the experimental data.

Key Words: Polycarbonate; Micro thermal imprinting; Viscoelastic model

1. Polymer in micro thermal imprint process

During the past couple of decades, micro- and nano-fabrication technology has been developed rapidly and a large number of research literatures have been published. Many precise fabrication technologies have been developed fast, such as nanoimprint lithography (NIL) process, Roll-to-Roll (R2R) imprinting process and so on [1, 2]. In these manufacturing technologies, thermal imprint process of amorphous glass polymer (PC or PMMA) for micro/nano pattern replication has been widely used in many areas, such as optical parts, solar energy, bio-mechanical and chemical chips, and so on.

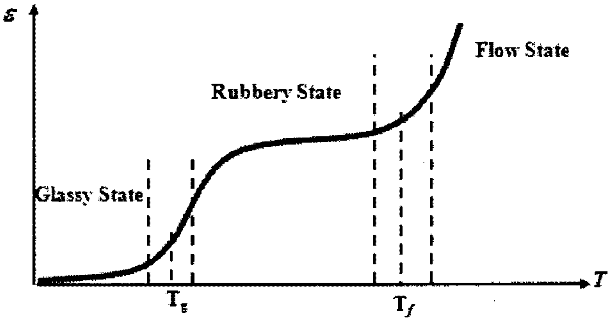

Fig. 1 Material deformation versus temperature in three states

It is known that the material property of amorphous polymer is strongly dependent on the conditions, such as temperature and loading. The material deformation behavior of amorphous polymer resists is a function of temperature can be classified into three states, as shown in

---

1. 아주대학교, 상해교통대학교
2. 한국생산기술연구원
3. 국립충주대학교
4. 아주대학교, 기계공학부
5. 미시건대학교
교신저자, E-mail: moongulee@ajou.ac.kr

Fig. 1 [3]. The micro thermal imprint process is operated near the glass transition temperature.

In this paper, we first measured the viscoelastic properties of a polymer material and estimate the parameters to establish the numerical model by performing tensile stress relaxation tests near T_g and further validation of the model and parameters was performed by comparing the simulation results to the experimental data.

2. Viscoelastic material model of polymer

For a viscoelastic polymer, the stress relaxation behaviour can be represented by the generalized Maxwell model with N Maxwell units (a spring and a dashpot in series) in parallel with an isolated spring. Additionally for the cross-linked polymer, one of the Maxwell units is replaced by a spring since the stress would decay to finite value rather than zero, as shown in Fig. 2 [4].

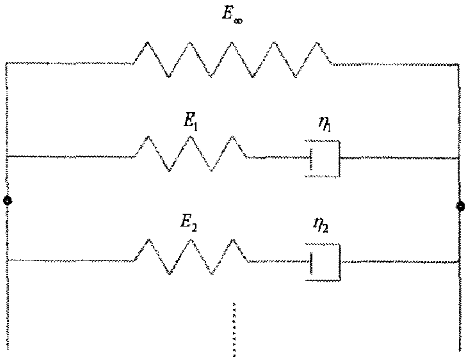

Fig. 2 Schematic diagram of viscoelastic model

The constitutive behavior can be expressed in the stress relaxation form:

$$\sigma(t) = \varepsilon_0 E(t) + \int_0^t E(t-\xi)\frac{d\varepsilon(\xi)}{d\xi}d\xi \qquad (1)$$

where σ(t) is stress, ε_0 is the initial value of strain and t and ξ represent current and past time, respectively. $E(t)$ is relaxation modulus. Its time dependence, also called stress relaxation function, can be expressed as an exponential series:

$$E(t) = E_\infty + \sum_{i=1}^{N} E_i \exp(\frac{-t}{\lambda_i}) \qquad (2)$$

$$E_0 = E_\infty + \sum_{i=1}^{N} E_i \qquad (3)$$

where E_0 is the instantaneous modulus, E_∞ is the equilibrium value of $E(t)$ after the time t goes to infinity. λ_i and E_i are relaxation modulus and time constant of the ith element in generalized Maxwell model, respectively. N is the number of Maxwell units. Divided by the instantaneous modulus E_0 at both sides, Eq. (2) and (3) can be converted to a dimensionless form in Eq. (4). This is the normalized stress relaxation function.

$$e(t) = 1 - \sum_{i=1}^{N} e_i (1 - \exp(\frac{-t}{\lambda_i})) \qquad (4)$$

$$1 = e_\infty + \sum_{i=1}^{N} e_i \qquad (5)$$

Temperature dependence is another prominent characteristic of the viscoelastic property. Based on the time-temperature superposition principle, the effect of temperature T on the material behavior is introduced through the dependence of the instantaneous stress σ_0 on temperature and through a so-called reduced time concept [5]. The expression of Eq. (1) can be rewritten as:

$$\sigma(t,T) = \int_{-\infty}^{t} E^{T_0}\left(\frac{t-\xi}{A(T)}\right)\frac{d\varepsilon(\xi)}{d\xi}d\xi \qquad (6)$$

where $A(T)$ is the time reduction factor at temperature T relative to the reference temperature T_0 and E^{T0} is the modulus at reference temperature T_0.

It is essential and beneficial that predict the material response at temperature T based on the response function at a reference temperature T_0. Based on the reduced time concept, the relationship between modulus at temperature T and T_0 can be expressed as Eq. (7). Using the Williams–Landel–Ferry (WLF) equation, the time reduction factor for materials can be expressred as the Eq. (8).

$$E^T(t) = E^{T_0}(t/A(T)) \qquad (7)$$

$$\log(A(T)) = -\frac{C_1(T-T_0)}{C_2+(T-T_0)} \qquad (8)$$

where C_1 and C_2 material constants at the reference temperature T_0 [6]. Then of the model enable us not only to predict the viscoelastic property of a glassy polymer, but also to analyze the process via the numerical simulation.

3. Experimental setup to establish material model

In order to investigate the viscoelatic property of glassy polymer near the glass transition temperature, the tensile stress relaxation test was chosen because the strain is small, the sample does not deform seriously and uniaxial force can be measured precisely in the transition region of our experimental setup.

The polymer specimens in the experiments are PC with glass transition temperature T_g equal to about 150 ℃, provided by Arystal. co. Ltd [7]. The samples were cut into a shape in Fig. 3. The tests were performed using a material testing system (MTS 810 FlexTest™) equipped with a model 653.02 high temperature furnace with 1 °C heating resolution and highest temperature up to 1400°C that can heat specimen to a specific temperature and hold in an approximate isothermal environment.

The finite element (FE) model of tensile relaxation tests was built using a commercial FE code, ABAQUS/Standard. The specimen is modeled as a viscoelastic material. The material parameters in the equations were obtained by performing preliminary tensile stress relaxation tests at 150 ℃.

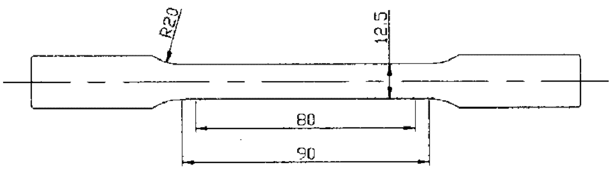

Fig. 3 Specimen shape for material test

4. Results and discussions

A number of preliminary tensile stress relaxation tests were carried out at 150 ℃ and at different instantaneous strain to produced stress relaxation curves. These curves were used to estimate model parameters. A normalization process was performed by dividing the measured stress in function of time $\sigma(t)$ of the initial stress σ_0. In the the tensile stress relaxation test, the ratio of measured force $F(t)$ and initial force F_0. The normalized stress relaxation function, $e(t)$ is also the ratio of reduce modulus $E(t)$ and instantaneous modulus E_0.

The parameters of the previously described generalized Maxwell model were calculated by the regression analysis of the stress relaxation curve, using the Levenberg-Marquardt (LM) algorithm combining with Universal Global Optimization (UGO) based on the 1stOpt (First Optimization) tool [8]. The normalized relaxation modulus and corresponding time constant were obtained for $N = 4$, as shown in Table 1.

Table 1 Parameters of the Generalized Maxwell model for PC at 150 ℃

N	e_i	λ_i
1	0.04309	0.06307
2	0.20989	4.05292
3	0.56332	33.160
4	0.15562	75.408

The material behavior at 150 ℃ was implemented into ABAQUS via viscoelastic material option to build viscoelastic material model and the glass transition temperature was set as a reference temperature. Then numerical simulation of tensile stress relaxation test was performed. The comparison result of the experiment and simulation at 150 ℃ is shown in Fig. 4. The simulation result agrees with the experimental data well, and this shows that such model parameters are feasible while the temperature at 150 ℃.

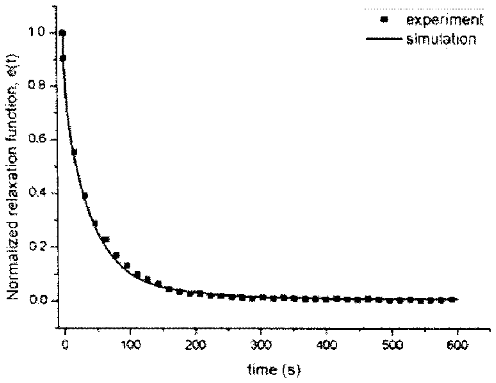

Fig. 4 Comparison of stress relaxation btn experiment data and simulation results at 150 ℃

In order to verify that the proposed viscoelastic model with set of parameters is feasible for FE analysis under different temperature conditions, further comparisons between FE simulation results and experimental data were carried out. Tensile stress relaxation tests at temperature of 155 ℃, 160 ℃ and 165 ℃ were performed. Based on a set of WLF time reduction factors obtained from the experiment data (C_1=7.2, C_2=88.5) at the polymer' s behavior is also predicted using the viscoelastic model at temperatures of 155 ℃, 160 ℃ and 165 ℃. Comparisons of the simulation results and experiment data are shown in Fig. 5.

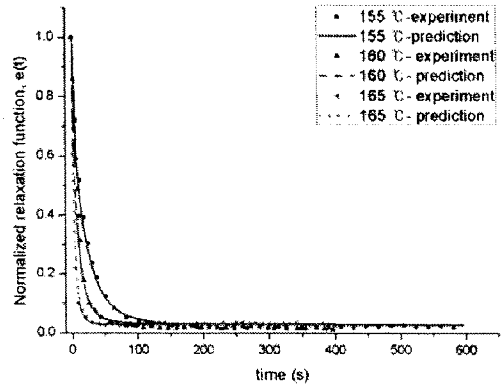

Fig. 5 Comparison of stress relaxation btn experiment data and simulation results

5. Conclusion

Experimental and numerical investigation on the deformation property of a glassy polymer PC near the glass transition temperature was performed and the feasibility of viscoelastic model for PC near T_g for micro thermal imprint process was verified. A viscoelastic material model based on the generalized Maxwell model is obtained by performing a series of stress relaxation tests and model parameter estimations at T_g. The model parameters were verified by comparing the simulation results to the experimental data. The simulation results using the obtained material parameters fitted to the experimental data well. Therefore, the viscoelastic model is feasible to describe the deformation behavior of the PC with various temperature conditions near T_g in the micro thermal imprint process.

Acknowledgement

This research was financially supported by the Ministry of Knowledge Economy (MKE) and Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Strategic Technology.

References

[1] Chou SY, Krauss PR, Renstrom PJ. Imprint of sub-25nm vias and trnches in polymers. Appl Phys Lett 1995;67: 3114.

[2] Makela T, Haatainen T, Majander P, Ahopelto J. Continous roll to roll nanoimprinting of inherently conducting polyaniline. Microelectron Eng 2007;84:877-879.

[3] Guo LJ. Recent progress in nanoimprint technology and its applications. J Phys D Appl Phys 2004;37: 123-141.

[4] Show MT, MacKnight WJ. Introduction to Polymer Viscoelasticity. 1st ed. Hoboken, New Jersey: John Wiley & Sons;2005

[5] ABAQUS Inc. Documentation, version 6.7;2007.

[6] Williams M, Landel RF, Ferry JD. J Am Chem Soc 1954;77:3701.

[7] http:// www.arystal.co.kr

[8] http:// www.7d-soft.com