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Short Communication

Experimental and numerical study on the viscoelastic property of polycarbonate near glass transition temperature for micro thermal imprint process

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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 (T_g). Through 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 T_g 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 of the model and parameters was performed by comparing the analysis of FE model results to the experimental data. As a result, the feasibility of the established viscoelastic model for PC near T_g was confirmed and this material model can be used in FE analysis for the prediction and improvement of the micro thermal imprint process for pattern replication.

1. Introduction: 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, amorphous polymers have become important and essential materials, for example, PMMA as the resin film coated on the silicon substrate in nanoimprint lithography process, polycarbonate (PC) as the substrate where micro pattern is embossed in the micro hot emboss process. Thermal imprint process of amorphous glass polymer 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. For example, Shan et al. used micro thermal imprint process for the fabrication of optical switch fabrication [3]. Leech et al. used the process to fabricate micrographic elements on polypropylene substrate [4]. Charest et al. proposed a fabrication method using a hot-embossing process for preparing microtextured polymer substrates for cell growth and studied the response of osteoblast cells grown on these surfaces [5]. Chien applied the process to fabricate microfeatured fluidic platform used for DNA/RNA test [6].

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 Fig. 1 [7]. When the temperature is lower than the glass transition temperature T_g, it is glassy state, in which amorphous polymer acts like a hard and brittle solid glass. The deformation is reversible. As the temperature is increased, it goes to a rubbery state, in which the polymer acts like an incompressible or approximately incompressible rubber. From glassy state to rubbery state there is no strict temperature, "jumping point", however, there is a transition region. The temperature range of this transition region is from 5 °C to 20 °C, depending on the characteristic of the polymer [8]. From the transition region to the rubbery state, the polymer shows dual response of reversible and irreversible deformation for mechanical stress. This property is regarded as the so-called viscoelasticity. When the temperature is further increased, it goes to the flow state, in which the polymer melts and can be regarded as a viscous non-newtonian liquid. The material deformation is irreversible.

Unlike the thermal-type nanoimprint lithography, during which thin polymer layer (usually from tens to hundred nanometer) is coated and imprinted on the silicon substrate as a resist film and

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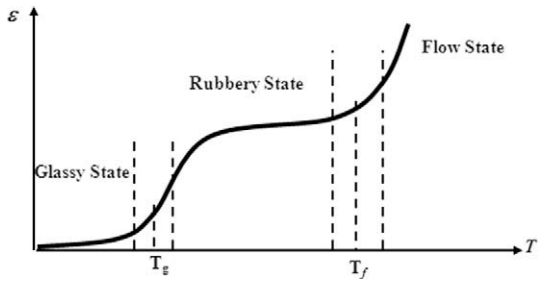

Fig. 1. Material deformation versus temperature in three states.

heated to a elevated temperature well above the glass transition temperature, the micro thermal imprint process in this study directly replicates the micro pattern structure from a mold or master to the surface of a hard or flexible polymer substrate. In order to minimize the process cycle time, the thermal stress in the materials, and also the replication errors due to the thermal expansion coefficients of mold and substrate, the imprinting temperature is generally set slightly above T_g, while the de-molding temperature is slightly below T_g. In other words, the operating temperature range is near T_g. It means that the glassy polymer in the thermal imprint process is at the transition region. Therefore, the polymer should be modeled as a viscoelastic material.

2. Viscoelastic material model of polymer

As mentioned previously, the micro thermal imprint process is operated near the glass transition temperature, at which the polymer behaves as a viscoelastic material. Under a constant load the material would undergo the two stages of deformation: an instantaneous elastic deformation at the very beginning followed by continual viscous deformation over a period of time. The viscous deformation results in decay of the applied load. This decay is relaxation. From the phenomenological standpoint, to the behavior can be described as a "mechanical analogy" model with a set of spring and dashpot components linked in series or parallel. The spring represents the elastic behavior and the dashpot represents viscous behavior. For a viscoelastic polymer, the stress relaxation behavior 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 crosslinked 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 [8].

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

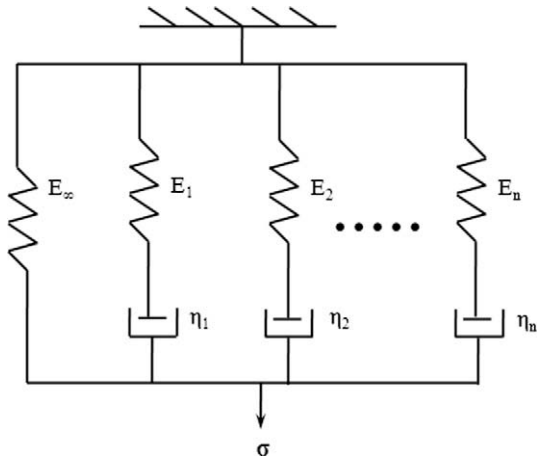

Fig. 2. Schematic diagram of viscoelastic model.

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

where $\sigma(t)$ 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:

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

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

where E_0 is the instantaneous modulus, E_∞ is the equilibrium value of $E(t)$ after the time t goes to infinity. E_i and λ_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, Eqs. (2) and (3) can be converted to a dimensionless form in Eq. (4). This is the normalized stress relaxation function.

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

$$1 = e_\infty + \sum_{i=1}^{N} e_i \tag{5}$$

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 [9]. The expression of Eq. (1) can be rewritten as:

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

where $A(T)$ is the time reduction factor at temperature T relative to the reference temperature T_0 and E^{T_0} 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 expressed as Eq. (8).

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

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

where C_1 and C_2 material constants at the reference temperature T_0 [10]. 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, as which will be described in the next section.

3. Experimental set-up to establish material model

In order to investigate the viscoelastic property of glassy polymer near the glass transition temperature, two kinds of transient tests can be used: stress relaxation test and creep test. In a stress relaxation test, an initial strain is instantaneously subjected to the sample and the stress necessary to maintain the constant strain is measured in a period of time. In a creep test, on the contrary, an initial stress is instantaneously subjected to the sample and then held constant in a period of time to measure the change in strain. 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 experi-