MODELLING MECHANICAL BEHAVIOUR OF AMORPHOUS POLY (L-LACTIC ACID) UNDER BIAXIAL STRETCH AT TEMPERATURES ABOVE GLASS TRANSITION

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Abstract

Stretch blow moulding process has been applied to manufacture of bioreosorbable vascular scaffold (BVS) made by poly (l-lactic acid) (PLLA) to improve the mechanical properties of product. Biaxial stretching test was conducted to obtain the mechanical properties of amorphous PLLA materials at temperatures above glass transition. The glass-rubber (GR) constitutive model was adopted to model the mechanical behaviour and can be used for the simulation for the forming process.

Introduction

The morphology of amorphous polymers can be changed by introducing biaxial stretch at temperatures above glass transition and with a subsequent fast cooling process. The mechanical properties of after-stretch materials can be improved a lot by this physical stretching process due to orientation of molecular chains and strain induced crystallization. For axisymmetric polymer products with closed cavity, stretch blow moulding is used to produce polymeric containers, bottles, etc. by taking advantage of this method. The preform is placed in a closed mold and temperature is increased to above the glass transition of materials. The axial stretch is conducted by drawing one end of the preform and circumferential stretch is introduced by pressurization with air internally.

Poly (L-lactic acid) (PLLA) is a kind of bioreosorbable polymer that has been widely applied in manufacturing medical implants. For the degradable properties, the bioreosorbable vascular scaffolds (BVS) have many advantages over the traditional bare metallic alloy scaffolds (BMS) or drug-eluting scaffolds (DES). However, a thicker strut of PLLA BVS always required to keep the same mechanical performance with the traditional ones. In order to overcome this bias, the stretch blow moulding process has been introduced for the manufacture of PLLA BVS [1].

In order to determine the process conditions in the stretch blow moulding process, like temperature, stretching speed, inside pressure etc., a lot of trial-and-error tests shall be required before the real industrial manufacture. The time and cost on this test can be greatly reduced by understanding the mechanical behaviour of polymer materials and simulating the deformation process with suitable constitutive model. This has been achieved successfully for predicting the shape evolution in the stretch blow moulding process of PET containers in the packaging industry by the glass-rubber (GR) model [2][3]. A similar mechanical response and constitutive behaviour related with temperature and strain rate have been found between PLLA and PET at temperatures above glass transition [4][5]. This paper shows the ability of the GR model to describe the mechanical behaviour of PLLA under biaxial stretch. The presented model can be future deployed for the simulation of stretch blow moulding process of PLLA materials for the manufacture of bioreosorbable vascular scaffold.

Experimental

Material and Sample Preparation

PLLA raw materials were extruded into thin films with thickness of 0.5mm by a single screw extruded. The DSC thermal analysis with heating rate of 10K/min was adopted to obtain the material properties of extruded films. The glass transition temperature (Tg) and temperature of cold crystallization (Tc) can be reached to get the temperature window for the biaxial deformation. By subtracting the contribution from cold crystallization, the initial crystallinity of PLLA films can also be reached to check its amorphous state. 75mm X 75mm square samples were prepared for the biaxial stretching test.

Biaxial Stretching Test

The mechanical properties of PLLA under biaxial stretch at temperatures above glass transition were tested by an in-house developed biaxial stretching machine in Queen’s University Belfast, which is shown in Figure 1. The PLLA square film sample was fixed by four groups of grips in the machine. The mechanism of the machine can provide a simultaneous biaxial stretch (EB), a constant-width stretch (CW) and sequential biaxial stretch (SB) by controlling the movement in two directions. The temperature of samples above glass transition was reached by forced convective heating transfer by two heaters at the top and bottom. The heating power of heaters were controlled by investigating the temperatures of the film by two thermocouples near the top and bottom surfaces of the film. Force load from stretch in the two directions was...
measured by two load cells on the grip of each axis. The real-time displacement and force data were recorded by a Labview interface on a computer. The EB deformation is reached at two strain rate of 1s\(^{-1}\) and 4s\(^{-1}\) at temperatures above glass transition. An ink mark is also made on each samples to guarantee a homogeneous deformation during the stretching process.

![Figure 1. Biaxial stretching machine](image)

**Constitutive Model**

**Glass-rubber (GR) Model**

The glass-rubber model developed by Buckley [6, 7] and implemented by Adams [8] can be was adopted. The total stress tensor \(\sigma\) consists of a bond-stretching stress \(\sigma^b\) and a conformational stress \(\sigma^c\) by equation (1).

\[
\sigma = \sigma^b + \sigma^c \quad (1)
\]

In the principal direction the stress balance for the total stress can be expressed as equation (2) and (3) in three directions.

\[
\sigma_i = s_i^b + K^b \sum_{j=1}^{3} e_j + \sigma^c(i) \quad (i = 1,2,3) \quad (2)
\]

\[
s_i^b = \sigma_i^b - \frac{1}{3} \sum_{i=1}^{3} \sigma_i^b \quad (3)
\]

Where, \(s_i^b\) is deviatoric stress, \(K^b\) is bulk modulus and \(e_j\) is principal natural strain.

The bond-stretching part has Hooke elasticity and non-Newtonian viscosity that can be express as equation (4).

\[
2G^b \frac{d\sigma_i^b}{dt} = \frac{d\sigma_i^b}{dt} + \frac{s_i^b}{\tau} \quad (i = 1,2,3) \quad (4)
\]

Where \(G^b\) is shear modulus and \(\tau\) is relaxation time, which is defined as \(\tau = \frac{\mu}{2G^b}\) and \(\mu\) is shear viscosity.

The nonlinear effect for the viscous part is incorporated into relaxation time \(\tau\) by equation (5), where the effects of evolution from stress \((a_{\sigma,j})\), structure \((a_{s,j})\) and temperature \((a_T)\) are considered.

\[
\tau = a_{\sigma,j} a_{s,j} a_T \tau^* (j = 1,2,3) \quad (5)
\]

The conformational part has hyper-elasticity and non-Newtonian viscosity that can be express as equation (6).

\[
\frac{d\varepsilon_i^c}{dt} = \frac{1}{\lambda_i^n} \sum_{j=1}^{3} C_{ij}^c \frac{d\sigma_j^c}{dt} + s_i^c(i = 1,2,3) \quad (6)
\]

Where \(\lambda_i^n\) is invariant of the network stretch, \(\gamma\) is conformational viscosity and \(C_{ij}^c\) is the tangent conformational compliance matrix that can be obtained from the Edwards-Viligis model by equation (7) and (8), which consider the contribution of hyperelasticity from slip-links.

\[
A^c = \frac{N_s k_b T}{2} \left(1 + \eta \left(1 - \alpha^2\right) \sum_{i=1}^{3} \frac{\lambda_i^2}{\lambda_i^n} \right) \mid (7)
\]

\[
\sigma_j^c = \frac{1}{\det \Lambda} \frac{\partial A^c}{\partial \ln \lambda_i} \quad (8)
\]

Where \(A^c\) is strain energy function, \(N_s\) is number density of slip-links, \(k_b\) is Boltzmann constant, \(\eta\) is freedom of movement of slip-links, \(\alpha\) is the degree of inextensibility of chains, \(\Lambda\) is the volume change during the deformation process, \(\lambda_i\) is the eigenvalues of left stretch tensor. More details on the constitutive model can be found on the reference [6, 7, 8].

**Numerical Solution**

The parameters in the model were calibrated based on a step-by-step method [8]. By dividing the stress into bond-stretching part and conformational part, the
parameters with corresponding physical meaning can be deduced from the experimental data. By Figure 2, the PLLA film after biaxial stretch in the experimental test shows that there was a perfect homogeneous deformation along the whole surface. By the incompressibility of PLLA materials during stretch in Figure 3, the deformation characteristics with reference to the initial coordinate system (X, Y, Z) can be expressed in Table 1.

![Figure 2. After-stretch PLLA film](image)

![Figure 3. Biaxial stretching process](image)

**Table 1. Deformation characteristics of PLLA films under biaxial stretch**

<table>
<thead>
<tr>
<th>Items</th>
<th>Symbols</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>x</td>
<td>$\Lambda(t)X$</td>
</tr>
<tr>
<td>Width</td>
<td>$y'$</td>
<td>$\Lambda(t)y'$</td>
</tr>
<tr>
<td>Thickness</td>
<td>z</td>
<td>$\frac{1}{\Lambda(t)^2}Z$</td>
</tr>
<tr>
<td>Deformation tensor</td>
<td>F</td>
<td>diag$\left(\Lambda, \Lambda, \frac{1}{\Lambda^2}\right)$</td>
</tr>
<tr>
<td>Velocity gradient tensor</td>
<td>L</td>
<td>diag$\left(\frac{\dot{\Lambda}}{\Lambda}, \frac{\dot{\Lambda}}{\Lambda}, \frac{2\dot{\Lambda}}{\Lambda}\right)$</td>
</tr>
</tbody>
</table>

Where, $\Lambda(t)$ is stretch ratio at time $t$, $\Lambda = 1 + Kt$, $K$ is the nominal strain rate. An explicit integration method can be adopted to obtain the stress evolution under different strain rates by solving the above equations.

**Results and Discussion**

**Experimental Results**

The resulted thermal curve from DSC test for the PLLA films is shown in Figure 4. It shows that under the heating rate of 10K/min, the glass transition temperature at the middle transition is about 58°C and the temperature for onset of cold crystallization is about 100°C. The melting temperature at the peak point is about 152°C. So the temperature window for the biaxial stretch can be ranging from 70°C to 100°C.

![Figure 4. Thermal curve of PLLA films by DSC test](image)

The viscoelastic mechanical behaviour of PLLA materials under biaxial stretch at temperatures of 70°C, 80°C, 90°C and 100°C under two different strain rates of 1s⁻¹ and 4s⁻¹ are shown in Figure 5 and 6. It shows clearly that there is strong temperature dependence for the mechanical properties of PLLA materials at temperatures above glass transition. There is obvious difference for the stages of deformation during the temperatures ranging from 70°C to 80°C just above the glass transition. An initial stiff response happens at the temperature of 70°C. Bigger yielding stress is required at higher strain rate. The difference of initial responses at different temperatures becomes smaller at higher temperature points. A stress flowing area exists at higher temperatures with slow increase of stress with the increment of strain. The higher the temperature is, the larger strain it is required for the arrest of this flowing phenomenon. A dramatic strain hardening happens after certain stretch. Bigger strain rate causes an early start of this strain-hardening behaviour.

**Modelling Results**

The GR model with parameters calibrated from experimental data is used to simulate the mechanical behaviour of PLLA materials above glass transition. The modelling results and testing results are compared in
Figure 7 and Figure 8. The temperature dependence at two strain rates can be both simulated very well by this model. The initial stiff response at temperature of 70°C was given and in good correspondence with the testing data. At temperature of 80°C to 100°C, an earlier strain hardening happens from the modelling than the real test at strain rate of 1s⁻¹. But the effect at strain rate of 4s⁻¹ disappeared and a good agreement can be found.

Conclusions

The viscoelastic mechanical behaviour of amorphous PLLA materials under biaxial stretch was investigated at temperatures above glass transition at two strain rates. Strong temperature and strain rate dependence can be found for PLLA materials. The GR model was adopted to simulate the deformation characteristics at the different process conditions. A good agreement was found between the results from experiment and numerical simulation by charactering the material parameters in the model. In the next step, the model can be used for the simulation of stretch blow moulding process to understand and optimize the processing conditions for the manufacture of PLLA BVS.

References