Computer Modeling on the Effect of the Multistep Nanoimprinting Process in Elastic Deformation Recovery of COC (Cyclic Olefin Copolymer)

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Abstract. The effect of the multistep imprint in elastic deformation recovery was studied numerically with more than one roll and different depth ratios. As well as effect hold-on time on the elastic deformation recovery of polymer Cyclic Olefin Copolymer (COC) material was studied using Generalized Maxwell (GM) constitutive model and their parameters in finite element simulation software of ABAQUS were presented. Firstly, the modified Genetic Algorithm (GA) was employed to obtain a Prony series of the viscoelastic model in terms of experimental data of the complex modulus for COC. To evaluate the elastic recovery of the microstructure, the cross-sectional area of micro-channel before and after hot-imprinting was computed and compared numerically. The simulated results were analysed and clearly showed an improvement in the elastic recovery rate of the microstructure area as the multi-step of rolling was employed.

1. Introduction
Since 1996, several attempts have been subsequently made to study the methods of polymer flow during the imprinting process as Chou developed nanoimprint lithography [1]. Hot roll-to-plate imbossing process is a continuous forming method that is a promising means of forming the microstructures required in medical devices or so on. In the hot roller press forming process, the polymer material is firstly preheated to the forming temperature. The polymeric plate is pressed initially by rotation movement of rolling mold. Then, the cooling of the polymeric substrate is conducted before demolding. Finally, the load is then removed and the part separated from the mold (demolding).

Numerical methods were employed to simulate polymer flow during imprinting by Hirai and Song [2, 3]. Young analysed polymer flow using a viscous fluid model to predict the polymer flow behaviour during the imprinting [4]. Nanoimprint flow behaviour has been modelled by the coarse-grain method derived from the 3D Navier-Stokes equations, Galerkin finite element program and using MARC software based on the Moony-Rivlin model by Sirotkin, Rowland and Scheer sequentially [5,6,7]. The deformation behaviour of solid polymer was observed by two methods, synchronous observation and asynchronous analysis by Liu [8]. The mathematical non-linear model of the hot imprint process included three steps of heating, imprinting and demolding was done by
Narijauskaitė [9]. Rheological analysis of COC with application to hot imbossing for microfabrication made by Jena [10]. In 2018 Hongbo provides a reference and direction for the further explorations and studies of large-area micro/nanopatterning technologies [11].

The most famous process used in the hot imbossing process is the isothermal hot imbossing which the mold and polymer will be heated to the same temperature [8]. When the mold is released, it gradually separates from the surface of the sheet, the binding force on the polymer surface is reduced and the polymer material also experiences a phenomenon of volume expansion which will also lead to elastic deformation of the molded microstructure. Springback phenomenon in the NIL process is studied with the MD simulation and the mold geometry effect on Springback by Yang [12]. In 2015 Qu studied the effect of mesh on Springback in 3D finite element analysis of Flexible Microrolling [13].

The study of the constitutive model of viscoelastic materials has been a long time, but the few study of dynamic viscoelasticity to determine the discrete relaxation time spectrum by the Generalized Maxwell model and the effect of nanoimprinting parameters process in elastic deformation recovery are reported. The key to accurately describing the characteristics of viscoelastic materials in the process of forming simulation is the accuracy and reliability of the material parameters. In this paper, firstly the parameters of the viscoelastic material model were fitted at the different temperatures of 100°C, 110°C, 120°C, 13°C, and 140°C. Then the master curve of the TOPAS® COC material model was obtained in terms of the Williams-Landel-Ferry (WLF) shift function at a specific temperature. Then, the ABAQUS finite element analysis software was used to simulate the rolling hot-press molding. Finally, effect of multistep imprint and hold-on time on elastic deformation recovery was studied.

2. A viscoelastic model for the TOPAS® COC resist and Optimization of model parameters

The mechanical properties of polymer materials are both viscous and elastic at the same time in any case. When the temperature of the polymer body is above the glass transition temperature, its state status lays between the ideal elastomer and the ideal viscous body. Under these circumstances, the total stress includes the elastic and viscous stress as it is subjected to an external force, which can be described in viscoelastic model. In our study, the complex modulus based on the viscoelastic generalized Maxwell constitutive model is used to solve the model parameters of the material. 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, as shown in figure 1. And the Prony equation of the storage modulus \( E_s(\omega) \) and the loss modulus \( E_l(\omega) \) of the generalized Maxwell model in the frequency can be expressed as equation (1)[10].

\[
E_s(\omega) = E_\infty + \sum_{i=1}^{n} E_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad \text{and} \quad E_l(\omega) = \sum_{i=1}^{n} E_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}
\]

where \( \omega \) is the angular frequency domain, \( E_i \) and \( \tau_i \) are relaxation modulus and time constant of the i-th element in the generalized Maxwell model, respectively. If \( g_i \) is a dimensionless modulus which can be expressed as: \( g_i = E_i/E_0 \) and \( E_0 \) is the instantaneous modulus which can be expressed as:

\[
E_0 = \frac{E_\infty}{(1 - \sum g_i, \sum g_i)}
\]

where \( E_\infty \) is the equilibrium value of \( E(t) \) after the time \( t \) goes to infinity, now \( E_s(\omega) \) and \( E_l(\omega) \) also can be expressed as following equation (3).

\[
E_s(\omega) = E_0 [1 - \sum g_i] + E_0 \sum g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad \text{and} \quad E_l(\omega) = E_0 \sum g_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}
\]

According to the storage modulus \( E_s(\omega) \) and the loss modulus \( E_l(\omega) \), the complex modulus \( E^* \) can be obtained as:

\[
|E^*| = \sqrt{E_s^2 + E_l^2}
\]

Based on the reduced time concept, the relationship between modulus at temperature \( T \) and \( T_0 \) can be expressed as equation (5).

\[
E(T_0, t) = E(T, t_0, a_T)
\]

Using WLF equation, the time reduction factor for materials can be expressed as equation (6).

\[ f(t) = \exp\left(-\frac{t - t_0}{\tau_0}\right) \]
where \( C_1 \) and \( C_2 \) material constants at reference temperature \( T_0 \) [14]. The glass transition temperature \( T_g = 80^\circ \text{C} \) of TOPAS®RCOC was selected as the reference temperature, and the curves at 100°C, 110°C, 120°C, 130°C, and 140°C were translated to form master curve at 80°C, as shown in figure 2.

![Generalized Maxwell model](image1.png)

**Figure 1.** Generalized Maxwell model

![Complex modulus curve at 80°C](image2.png)

**Figure 2.** Complex modulus curve at 80°C

The viscoelastic model parameters were obtained by a genetic algorithm at the reference temperature (80°C). In table 1 fitting results are compared with the results at a reference temperature, and comparing results show that the fitting results are in good agreement with the experimental results.

| Prony series | \( \tau_i \) | \( E_i \) |
|--------------|-------------|---------|
| 1            | 1.00E-07    | 1.53E+07|
| 2            | 1.00E-06    | 8.97E+05|
| 3            | 1.00E-05    | 7.86E+05|
| 4            | 1.00E-04    | 1.68E+05|
| 5            | 1.00E-03    | 2.11E+05|
| 6            | 1.00E-02    | 9.61E+04|
| 7            | 1.00E-01    | 8.07E+04|
| 8            | 1.00E+00    | 3.23E+04|
| 9            | 1.00E+01    | 5.27E+04|
| 10           | 1.00E+02    | 1.62E+04|

Note: \( E_0 = 1.8E+1 \text{MPa} \)

**Table 1.** Dynamic viscoelastic model parameters obtained by genetic algorithm at 80°C [15]

3. **Simulations of the model in roll forming of Polymer TOPAS®COC**
   In the simulation, the mold is often defined as an analytical rigid body, and the polymer substrate is defined as a deformable body. This is because the mold is usually made of metal and its strength is far greater than the strength of the polymer material. In the paper, the polymer sheet is a rectangle with a 100 mm in length dimension and 1.5 mm in the thickness dimension.
In this paper, the polymer substrate was considered to be viscoelastic material and the basic physical parameters of polymer in tables 1-3. Roll forming is a combination of external force and boundary constraints. A constraint in the X, Y, and R3 directions is set on the bottom edge of the polymer sheet. In the analysis model, a displacement in the Y direction is first set at the reference point of the rolling mold centre. Then, the rolling mold starts to rotate and the thin plate is purely rolling. Constant rotational speed in the Z direction and a constant linear velocity in the X direction are set at the central reference point. The temperature field of the rolling die and the polymer sheet is defined in a predefined field. The transfer process is in a constant temperature environment, ignoring the heat transfer process. In this analytical model, the polymer sheet mesh type is CPE4RT and the total number of grids is 23872 see figure 3.

| Table 2. Material physical parameters of TOPAS® COC |
|---------------------------------|---------|
| Parameters                      | Values  |
| Density (10³kg/m³)              | 1.01    |
| Elastic modulus (MPa)           | 2600    |
| Poisson’s ratio                 | 0.3     |

Using the principle of translation, the complex modulus data at different temperatures are transformed by the shift factor tabulated in table 3.

| Table 3. WLF equation material constants |
|------------------------------------------|---------|
| Parameters                                | Values  |
| C₁                                        | 7.2     |
| C₂                                        | 88.5    |
| $T_0$                                     | 150°C   |

4. Results and Discussion

In this paper, the elastic recovery rate indicates the change of the elasticity of the microstructure, and the elastic recovery rate (φ) can be expressed as equation (7).

$$\varphi = \frac{A - A_R}{A}$$ (7)

where $A$ and $A_R$ are a microstructure cross-sectional area before and after the rebound, respectively.

4.1 Effect of the number of printing steps on recovery deformation of micro-structure

To study the effect of multi-step press on recovery deformation of micro-structure, there are several factors taken into account the imprint depth at each step and the cooling time. When the printing is done using two or three stages through three rollers. The polymer is firstly compressed by a certain
percent of imprint depth by the first roller and then roller releases the flat polymeric substrate which it continues to move to a specific position pressed by the second roller to the required depth for two-step process, as shown in figure 4.

The simulated imprint results of elastic recovery rate (\(\varphi\)) for three different processes of one-step, two-step and three-step tabulated in table 4. By comparison of these results of 5.60% in one step imprint process, 2.98% in two-step process and 2.00% in the three-step process, it is demonstrated that the elastic recovery rate decreases as the number of step increases. The reason is that with an increasing number of steps, larger energy loss to deform polymer and will result in small elastic recovery. Figure 5 clearly shows that the multi-step imprinting has a significant impact on the elastic recovery.

| No. | Multi-step ratio | Width/(mm) | Depth/(mm) | Area after the rebound | Area before the rebound | \(\varphi\) % |
|-----|------------------|------------|------------|------------------------|-------------------------|-----------|
| 1   | 0.5              | 1.00301    | 0.471099   | 0.742280               | 0.785398               | 5.60      |
| 2   | 0.3:0.2          | 1.012480   | 0.479123   | 0.761995               | 0.785398               | 2.98      |
| 3   | 0.15 :0.15:0.15  | 0.972328   | 0.503947   | 0.769693               | 0.785398               | 2.00      |

![Figure 5. Effect of the number of printing steps on recovery deformation of micro-structure](image)

4.2 Effect of the imprint depth ratio in the two-steps imprint process

The effect of the imprint depth ratio on recovery deformation of micro-structure, which the ratio is defined as the ratio of the imprint depth in the first step to its amount in the second step was studied and the results showed a remarkable effect. Figure 6 shows the change of the imprint depths versus...
time for different two-steps process, which illustrated the displacement change at the selected point A (shown in figure 3) with different imprint ratio from the beginning to the demold.

### Table 5. Effect of the imprint depth ratio on recovery deformation of micro-structure

| No. | Two step ratio | Width/(mm) | Depth/(mm) | Area after the rebound | Area before the rebound | φ %  |
|-----|----------------|------------|------------|------------------------|-------------------------|------|
| 1   | 0.3:0.2        | 1.01248    | 0.479123   | 0.761995               | 0.785398                | 2.98 |
| 2   | 0.2:0.3        | 1.01209    | 0.469291   | 0.746073               |                         | 5.01 |
| 3   | 0.35:0.15      | 1.00984    | 0.468767   | 0.743583               |                         | 5.32 |
| 4   | 0.15:0.35      | 1.00444    | 0.464366   | 0.732663               |                         | 6.71 |

The detailed elastic recovery rate (φ) with different imprint depth ratio is tabulated in table 5. It is found that the elastic recovery rate (φ) is 2.98 % at imprint depth ratio 0.3: 0.2 (0.3mm in depth at the first step and 0.2 mm at the second step) which is the least value achieved. The elastic recovery rate (φ) is 5.01 % if the imprint depth ratio is reversal with 0.2: 0.3. However, this rule is also applied to the imprint depth ratio of 0.35: 0.15, when the imprint depth at the first step is larger than that at the second step, will result in small elastic recovery.

![Figure 6](image_url)

**Figure 6.** The imprint depths during the two-steps imprint process with time

In addition, the imprint depth ratio for two-step process has a profound effect on the elastic recovery, as shown in figure 7. By using different imprint depth ratio through steps, the elastic recovery rate will be different. These imply that the imprint depth ratio and their order may have not negligible effect on elastic recovery.
4.3 Effect of the hold-on time on recovery deformation of micro-structure

The molding quality of the fabricated part is often influenced during the pressurization and demolding stages. To enable the polymer forming better in the hot press forming process, the requirements of the fine structure cavity and the efficient mold release are needed in general. Longer contact time between the rolling mold and polymer substrate provoked sufficient heat transfer before a demolding, which most likely enhanced the polymer cooling and will result in a decrease recovery deformation of micro-structure [16-17]. Table 6 shows the effect of hold-on time on the recovery deformation of micro-structure. It is observed that the value of the recovery deformation decreases as hold-on time increases as the hold-on time is less than 50 seconds. However, it is found that the value of the recovery deformation increases to 1.42% at 60 seconds of hold-on time and then the value of recovery deformation hold is kept as a steady value, as shown in figure 8.

![Figure 7. Effect of the imprint depth ratio on recovery deformation of micro-structure](image)

![Figure 8. Effect of the hold-on time on recovery deformation of micro-structure](image)
Table 6. Effect of the hold-on time on recovery deformation of micro-structure

| No. | Hold-on time/ (sec) | Width/(mm) | Depth/(mm) | Area after the rebound | Area before the rebound | $\varphi$ (%) |
|-----|---------------------|------------|------------|-------------------------|-------------------------|--------------|
| 1   | 0                   | 1.00301    | 0.471099   | 0.74228                 | 0.785398                | 5.60         |
| 2   | 50                  | 0.974171   | 0.513831   | 0.786397                | 0.785398                | 0.18         |
| 3   | 60                  | 0.966131   | 0.524901   | 0.798587                | 0.785398                | 1.42         |
| 4   | 70                  | 0.968133   | 0.524901   | 0.798238                | 0.785398                | 1.63         |

5. Conclusion
In the paper, the genetic algorithm (GA) was employed to obtain a Prony series of the viscoelastic generalized Maxwell model in terms of experimental data of TOPAS®-COC material. Using commercial nonlinear finite element software package of ABAQUS, a rolling hot forming model with different processes were established and simulated. Several conclusions can be made as follows: The effect of a multistep imprint on elastic deformation recovery is remarkable. To reduce elastic deformation recovery, the multistep processes are recommended. The imprint depth ratio for the two-steps imprint process and their sequencing have significant effects on elastic recovery. The mold quality of the fabricated part will be affected by hold-on time as well.

6. References
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