

## Role of Rheology on Quality of Polymeric Articles

Faezeh Aghazadeh<sup>1</sup>, Hossein Hosseini<sup>2</sup>, and Fardin Seyyednajafi<sup>1</sup>

<sup>1</sup> Centre of R&D, Tabriz Petrochemical Company, Tabriz, Iran

<sup>2</sup> Department of Chemical Engineering, University of Tabriz, Tabriz, Iran

### ABSTRACT

Polymer processing for production of all forms of polymeric articles has found a great place in chemical industries. A nonlinear viscoelastic rheological model is implemented for developing the process model. This model describes deformation process of a sheet in thermoforming process. Because of relaxation pause after plug-assist stage and also implementation of two stage thermoforming process have minor wall-thickness variation and consequently minor warpage and better mechanical properties of thermoformed articles. For model validation, a quantitative relation between stress and technical parameters of plug-assist thermoforming is determined by comparison of theoretical and experimental results.

### INTRODUCTION

Polymer processing for production of all forms of polymeric articles has found a great place in chemical industries. Thermoforming process is one of the most popular techniques in this field. It applies to thermoplastic sheet as a film-forming technique for various packaging applications such as medical devices, food containers, and pharmaceuticals [1-8]. Wide applications of thermoforming are due to its high performance, simplicity, compactness and relatively low-cost equipment. These issues make it possible to produce complex,

large-scale configurations and free form shapes of products. In thermoforming, a heated plastic sheet is stretched into a mould cavity by applying pressure and eventually direct mechanical loading are used [9,10]. Upon contacting of a sheet with the cold surface of the mould, the sheet deformation is terminated. The forming sequence induces a thickness variation in the final part. Besides wall-thickness variation, other problems facing the thermoforming industry are mainly physical instabilities during inflation – rupture of sheet and warpage exhibited in the final parts. There are many ways to stretch sheets: vacuum, air pressure and mechanical aids such as implementation of a plug. For increasing the quality of products such as narrow wall-thickness tolerance or elimination of frozen-in stresses, a combination of mechanical and vacuum or pressure forming methods may be implemented. The process initially involves the usage of mechanical pre-stretching with plug and then vacuum or pressure forming is applied. Figure 1 illustrates this process [11].

Since quality of final products is characterized by their minor wall-thickness variation, so evaluation of this property provides estimation to physical properties of polymeric products such as strength and toughness. Many researches have been carried out to investigate the thermoforming

process both analytically and numerically [11-16].

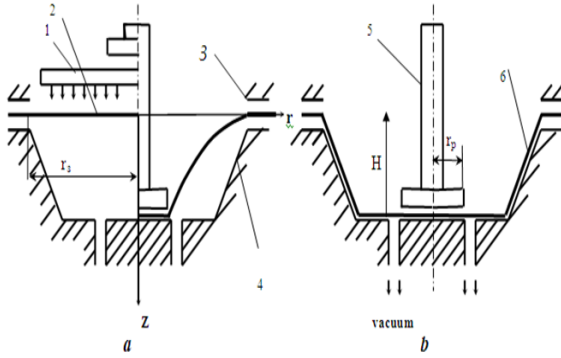


Fig. 1. Flow diagram of plug-assisted vacuum thermoforming (a - heater and plug-assist ; b - vacuum thermoforming ): 1 - heater, 2 - sheet prior to forming, 3 - clamp frame, 4 - mould, 5- plug, 6- deformed sheet.

However, there is lack of literature about deformation processes in thermoforming and its effect on wall-thickness uniformity and frozen-in stresses, there is a need for further research. Present study was conducted to simulate deformation processes in thermoforming processes.

### RHEOLOGICAL MODELLING

As mentioned above, warpage prediction is very important due to processing constraints. It may finally cause system failure. Proper description of the problem is directly dependent on the correct selection of an appropriate rheological model. Leonov developed a theoretical model in this area [17]:

$$\left\{ \begin{aligned} \bar{\sigma} + p\bar{\delta} &= 2\bar{c}W_1 - 2\bar{c}^{-1}W_2 \quad (1) \\ \bar{e}_f &= \frac{1}{\theta_0(T)G_0(T)} \cdot [f(I_1, I_2)]^\psi \cdot \left[ \left( \bar{c} - \frac{I_1}{3} \bar{\delta} \right) W_1^s - \left( \bar{c}^{-1} - \frac{I_2}{3} \bar{\delta} \right) W_2^s \right] \\ \frac{d\bar{c}}{dt} + \bar{w}\bar{c} - \bar{c}\bar{w} - \bar{c}(\bar{e} - \bar{e}_f) - (\bar{e} - \bar{e}_f)\bar{c} &= 0 \end{aligned} \right.$$

Where:

$\bar{\sigma}$  is stress tensor; P is Lagrange multiplier, determined by boundary condition;  $\bar{\delta}$  is identity tensor;  $\bar{c}$  is Cauchy strain tensor;  $\bar{e}_f$  is flow strain rate tensor;  $\bar{w}$  is vortex tensor;  $\bar{e}$  is strain rate tensor;  $\theta_0(T)$  is relaxation time; T is temperature;  $G_0(T)$  is tensile modulus; W is strain energy function  $W = W(I_1, I_2)$ ;  $I_1$  and  $I_2$  are primary and secondary strain tensor invariants respectively,  $\psi$  is dimensionless parameter ( $\psi = 0$  at  $\bar{w} = 0$  and  $\psi = 1$  at  $\bar{w} \neq 0$ );  $f(I_1, I_2)$  is dimensionless function that defines relaxation time, and  $2W^S = W(I_1, I_2) + W(I_2, I_1)$  represents the symmetric function of W.

The last one can be shown by:

$$\begin{aligned} W_1 &= \frac{\partial W}{\partial I_1} & W_2 &= \frac{\partial W}{\partial I_2} & W_1^S &= \frac{\partial W^S}{\partial I_1} \\ W_2^S &= \frac{\partial W^S}{\partial I_2} \end{aligned}$$

Tensors in equation (1) will be as follows:

$$\begin{aligned} \bar{e} &= \frac{\dot{\gamma}}{2} \cdot \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; & \bar{w} &= \frac{\dot{\gamma}}{2} \cdot \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \\ \bar{c} &= \begin{pmatrix} c_{11} & c_{12} & 0 \\ c_{12} & c_{22} & 0 \\ 0 & 0 & 1 \end{pmatrix}; & \bar{c}^{-1} &= \begin{pmatrix} c_{22} & -c_{12} & 0 \\ -c_{12} & c_{11} & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned} \quad (2)$$

Where  $\dot{\gamma} \equiv \frac{d\gamma}{dt} ::$  shear rate.

Now, with equations (2) and for pure shear process ( $\frac{dc_{ij}}{dt} = 0$ ), the second and third equations of system equations (1) will be as

follows:

$$\left\{ \begin{array}{l} c_{11}^2 - c_{11} \cdot c_{22} + 2c_{12}^2 = 4\dot{\gamma} \cdot \theta_0(T) \cdot F(c_{12}) \cdot c_{12} \\ c_{12} \cdot (c_{11} + c_{22}) = 2\dot{\gamma} \cdot \theta_0(T) \cdot F(c_{12}) \cdot c_{22} \\ c_{22}^2 - c_{11}c_{22} + 2c_{12}^2 = 0 \end{array} \right. \quad (3)$$

where

$$F(c_{12}) = \exp \left[ (\beta - 7.8\sqrt{1-c_{12}^2}) \left( \frac{1}{\sqrt{1-c_{12}^2}} - 1 \right) \right]$$

From solving of equations system (3) we will have:

$$\dot{\gamma} = \frac{I}{\theta_0(T) \cdot F(c_{12})} \cdot \frac{c_{12}}{I - c_{12}^2} \quad (4)$$

But in practice there is a problem for application of Eq.(1). This problem arises due to the choice of selecting strain energy function  $W = W(I_1, I_2)$ . Most researchers use Mooney-Rivlin potential, but there are differences between experimental and theoretical results for prediction of stress and strain. Results of recent research show that in various kinematical deformations, the following potential can be used [18]:

$$W = 0.25G_0(I_1 + I_2 - 6) \quad (5)$$

From the first equation of the Rheological model (1) with condition (5) and elastic tensors in equation (2), following equation for stress can be developed:

$$\sigma_{12} = G_0(T) \cdot c_{12} \quad (6)$$

By using the strain energy function presented in Eq. (5), in conjunction with the model in Eq. (1), a mathematical description for the deformation process occurring in thermoforming can be developed.

## RHEOLOGICAL PARAMETERS AND DEFORMATION PROCESSES

Consider a polymeric sheet with radius ( $r_3$ ) is heated for production of an axisymmetric article. It is deformed by movement of a plug with radius of  $r_p$  at constant velocity  $V_p$ , in direction of “z” axis. The implemented material is assumed to be incompressible and isotropic. The deformation process is carried out under isothermal condition. The deformed sheet could be considered a thin shell, thus the hot polymer can be modelled as a membrane. Therefore, the bending resistance of the hot sheet is ignored and the material thickness is assumed to be small in comparison to dimensions of the material. Three different stretch ratios involving in deformation process are as follows:

$$\lambda_1 = \frac{d\xi}{d\xi_0}; \lambda_2 = \frac{r}{r_0}; \lambda_3 = \frac{h}{h_0} \quad (7)$$

where  $\lambda_1, \lambda_2$  and  $\lambda_3$  are the principal stretch ratios in the meridional, radial and thickness directions of the membrane, respectively. They are related together by the incompressibility condition  $\lambda_1 \lambda_2 \lambda_3 = 1$  and  $\xi, \xi_0$  are length of meridian in deformed and strainless sheet.

$r, r_0$  :: radii of deformed and strainless sheet, respectively.

$h, h_0$  :: thickness of the sheet after and before deformation, respectively.

Mechanical pre-stretching is a planar stretching (pure shear). Therefore, the following conditions exist:

$$\lambda_2 = 1; \sigma_3 = 0; \lambda_3 = \lambda_1^{-1} \quad (8)$$

With respect to the conditions and the tensors in equation (1), the following expression can be written:

$$\bar{\varepsilon} = \dot{\varepsilon} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \bar{\omega} = 0;$$

$$\bar{c} = \begin{pmatrix} c & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & c^{-1} \end{pmatrix}; \bar{c}^{-1} = \begin{pmatrix} c^{-1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & c \end{pmatrix}$$

(9)

where  $\dot{\varepsilon} ::$  rate of deformation in longitudinal direction.

The primary and secondary invariants of tensor  $\bar{c}$  are resulted from equation (9) as:

$$I_1 = I_2 = c + 1 + c^{-1} \quad (10)$$

By utilizing equations (9) and (10), following form of equation (1) can be developed.

$$\bar{\sigma} + p\bar{\delta} = 0,5 G_0(T) \cdot \begin{pmatrix} c - c^{-1} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & c^{-1} - c \end{pmatrix} \quad (11)$$

$$\bar{\varepsilon}_f = \frac{1}{4\theta_0(T)} \exp[-\beta(c + c^{-1} - 2)] \cdot \begin{pmatrix} c - c^{-1} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & c^{-1} - c \end{pmatrix} \quad (12)$$

Parameter  $p$  is resulted from condition (8):  $\sigma_3 = 0$ . By substituting expressions (9) and (12) into equation (1):

$$\frac{dc}{dt} = 2 \left[ \dot{\varepsilon} \cdot c - (c^2 - 1) \frac{1}{4\theta_0(T)} \exp[-\beta(c + c^{-1} - 2)] \right] \quad (13)$$

This differential equation defines kinetics of elastic strain during the deformation process of viscoelastic media. The deformation rate is defined as follows:

$$\dot{\varepsilon} = \frac{d\varepsilon^H}{dt} = \frac{d \ln \lambda}{dt} = \frac{1}{\lambda} \frac{d\lambda}{dt} \quad (14)$$

where  $\varepsilon^H$  is Hencky strain.

There are two different strains:

1) Total strain (viscous and elastic deformations)

$$\varepsilon^H = \frac{1}{2} \ln \left[ \left( \frac{\tilde{r}}{a} \right)^2 + 1 \right] \quad (15)$$

2) Elastic strain  
( $\varepsilon^H_e$ ):  $c \equiv \lambda_e^2 = \exp(2\varepsilon^H_e)$  (16)

$$\text{where } a \equiv \tilde{r}_1^2 \frac{r_3}{V_p \theta_0(T)} \cdot \frac{1 - \tilde{r}_p}{\tilde{r}_p};$$

$$\tilde{r} \equiv \frac{t}{\theta_0(T)}.$$

Finally, from equation 11 and condition shown by equation 4 following relationship can be derived.

$$\sigma_I \equiv \sigma = G_0(T) \cdot (c - c^{-1}) \quad (17)$$

For describing deformation process at any moment of thermoforming the following conditions can be used (see figure 2).

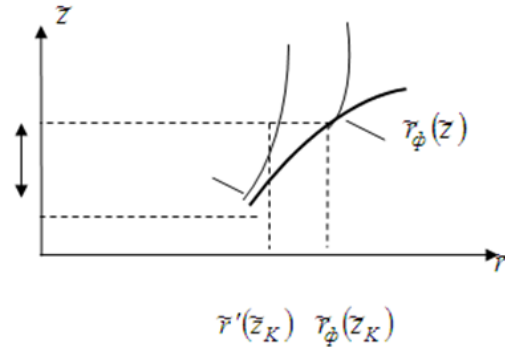


Fig. 2. Deformation process sketch of sheet during thermoforming;  $\tilde{r}'(\tilde{z})$ - sheet profile in beginning of the process;  $\tilde{r}(\tilde{z})$ - the profile at the end of the process;  $\tilde{r}_\phi(\tilde{z})$ - mould surface profile.

$$\text{at } \tilde{z} = \tilde{z}_K : \tilde{r} = \tilde{r}_\phi(\tilde{z}_K), \theta = \theta_\phi(\tilde{z}_K),$$

$$\lambda_1 = \lambda'_1(\tilde{z}_K), \lambda_2 = \lambda'_2(\tilde{z}_K) \frac{\tilde{r}_\phi(\tilde{z}_K)}{\tilde{r}'(\tilde{z}_K)} \quad (18)$$

where:

$\tilde{r}_\phi(\tilde{z})$  :: profile equation in corner surface of the mould,

$$\theta_\phi = \text{arccotg}\left(-\frac{d\tilde{r}_\phi}{d\tilde{z}}\right),$$

$\lambda'_1(\tilde{z}), \lambda'_2(\tilde{z})$  :: stretch-ratios in the previous deformation adjoin phase,

$\tilde{r}'(\tilde{z})$  :: function of sheet surface profile in the previous adjoin phase,

Quality criteria for wall-thickness variation can be defined as:

$$\delta = 1 - \frac{h_{\min}}{h_{\max}} \quad (19)$$

where  $h_{\min}$  and  $h_{\max}$  are the minimum and maximum wall-thickness of product, respectively.

As non-uniform variations of polymeric sheet thickness during plug-assist vacuum forming process occurs in the both first and second stages, the final distribution function of wall-thickness using Eq. (18) and considering incompressibility of polymer ( $\lambda_1\lambda_2\lambda_3 = 1$ ) it takes the following form.

$$h(\tilde{r}_\phi) = \frac{h_1(\tilde{r}_1)}{\lambda_1(\tilde{r}_\phi)\lambda_2(\tilde{r}_\phi)} \quad (20)$$

where  $\tilde{h}_1(\tilde{r}_1)$  is function of wall-thickness distribution in polymeric sheet at the end of plug-assist process.

By using the second relationship in Eq. (7), Eq. (20) can be modified to:

$$\tilde{h}(\tilde{r}_\phi) \equiv \frac{h(\tilde{r}_\phi)}{h_0} = \frac{1}{\sqrt{1+b\left(\frac{\lambda_2(\tilde{r}_\phi)}{\tilde{r}_\phi}\right)^4 \lambda_1(\tilde{r}_\phi)\lambda_2(\tilde{r}_\phi)}} \quad (21)$$

where:

$h_0$  :: initial thickness of the polymeric sheet,

$$b \equiv \lambda^2(z=0) - 1.$$

## RESULTS AND DISCUSSION

Variation of stress versus shear rate can be seen in figure 3 for ABS-sheet at temperature  $T=140^\circ\text{C}$ . There is a good agreement between theoretical results from equations (4 -6) and experimental results (points).

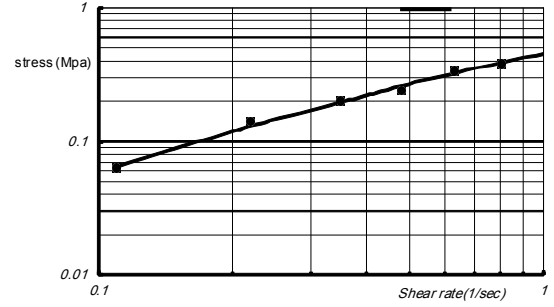


Figure 3. variation of stress vs. shear rate for ABS at  $T=140^\circ\text{C}$ .  $\beta=3.55$ ,  $G_0 = 0.635\text{ MPa}$ ;  $\theta_0 = 0.3\text{ sec}$ . (—): equation 4; points: experimental data.

Figure 4 shows kinetics of development of total and elastic strains. As shown there is a good agreement between theoretical (Eqs. 15 and 16) and experimental data for ABS at  $T=140^\circ\text{C}$ .

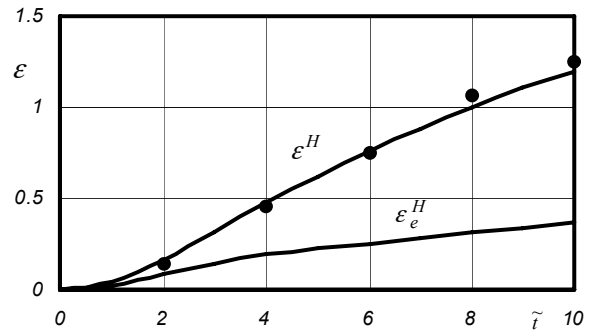


Figure 4. Kinetics of development of total and elastic strains for ABS sheet. (—) theoretical model; points: experimental data.  $\beta=3.55$ ;  $\theta_0 = 0.3\text{ sec}$ ;  $a=3.16$ .

By implementing Eq. (21), wall-thickness distribution for whole sheet can be determined. For evaluation of the theoretically developed model, simulated

wall-thickness distribution is compared with the experimental one (figure 5). The experimental data are for ABS sheet that is used widely in various industries such as food packaging. As shown, the theoretical and experimental results demonstrate a very satisfactory agreement.

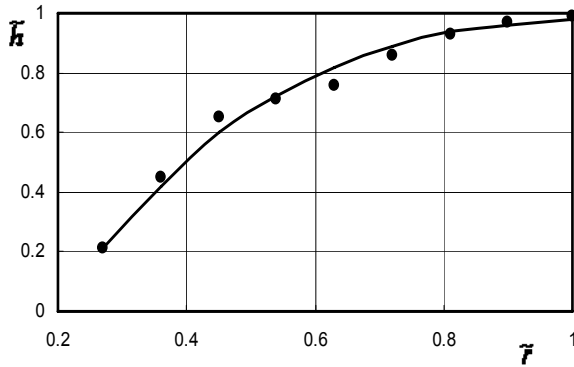


Figure 5. Comparison of model simulation from equation 21 (—) and experimental (●) wall-thickness distribution for ABS ( $h_0 = 1\text{mm}$ ).

The following calculation method enables us to have a quantitative evaluation of product quality even at designing step. Followings are required data in order to perform this method:

- Geometric parameters of product such as radius of sheet and depth of the article.
- Thickness of the used polymer sheet.
- Obtained results out of thermoforming process modelling, according to the description of deformation processes mentioned at the beginning of this paper.
- Relaxation time and flexibility parameter of macromolecular chains.
- Allowable wall-thickness variation of article.

By the use of above-mentioned information, it is possible to find following results:

- It is possible to specify accumulated stresses in meridional and radial directions at plug-assisted stage and

by results of deformation process modelling.

- To find  $h(\tilde{r}_\phi)h_{(r_0)}$  equation and then we have minimum & maximum amounts of thickness.
- To calculate wall-thickness distribution by equation 19.
- It is possible to guarantee product quality by comparing obtained with allowable wall-thickness variation which may be specified by the manufacturer.
- To calculate total and elastic strains for preventing from sheet fracture during thermoforming process.
- To find variation of stress versus shear rate at any moment of thermoforming process for preventing from warpage during application of polymeric articles.

By using of presented mathematical model in this paper it is not only possible to estimate wall-thickness distribution of product but also evaluate the kinetics of thermoforming process when necessary. It is important when we want to stop the deformation process at special points of mould level at vacuum forming stage. For solving this problem, it is necessary to specify only the mutual relation between boundary contact points of polymer sheet, mould surface and deformation process time. There is the following equation for vacuum thermoforming time.

$$t_{proc} = \frac{V_{arti} - V_{zag}}{\mu' \cdot s \sqrt{RT} \frac{2k}{k+1}} \left( \frac{k+1}{2} \right)^{\frac{1}{k-1}} \quad (22)$$

where:

$t_{proc}$  :: vacuum thermoforming process time,

$V_{iz}$  :: volume of polymer article,

$V_{zag}$  :: volume of polymer sheet after plug-assist,

$K$  :: adiabatic coefficient of exit gas from mould hole,

$T$  :: gas temperature,

R :: gases constant,

S :: total cross section levels of current holes on mould,

$\mu$  :: dimensionless coefficient which is a sign of gas consumption in thermoforming equipments (0.4 – 0.6).

It is necessary to have volume differences for any usage of above-mentioned formula which is obtainable easily by the following equation:

$$V - V_{zag} = \pi \left[ \int_0^{z_k} r_{\phi}^2(z) dz + \int_{z_k}^H r^2(z) dz - \int_0^H r_1^2(z) dz \right] \quad (23)$$

where:

$r_{\phi}(z)$  :  $r_{\phi}(z)$ : profile equation of side surface of mould,

$r(z)$  :  $r(z)$ : profile of sheet surface at vacuum stage,

$z_k$  :: coordinates of boundary contact points of sheet with side surface of mould,

H :: depth of polymer article,

$r_1(z)$  :  $r_1(z)$ : sheet profile equation after plug-assist stage.

Now, it is possible to have a suitable relation for kinetics of thermoforming process by equations of 22 and 23.

It is well known that the stage of vacuum-forming with a pre-stretched sheet occurs too quickly for experiencing of relaxation processes in the polymeric sheet. This will result in this fact that almost all accumulated deformations in polymeric sheet within this stage are elastic. Consequently, the minimization of the accumulation may be realized only by minimizing of the general deformations accumulated in polymeric sheet during this stage. For practical purposes, this means that the profile of the pre-stretched sheet should be maximally approximated by the profile of the final product which could be assured based on the application of a plug with the respective radius.

In contrast to the second stage, the stage of plug-assisted can be regulated in the

sense that it is technically possible to control the motion of the plug. This creates a practical opportunity that at this stage to organize the relaxation process of elastic deformations accumulated in a polymeric sheet during the process of plug-assist forming. The essence of the simplest of many variants used in the realization of this process lies in the creation of a relaxation pause period between the first and the second stage. During this period the accumulated elastic deformations are completely or partially relaxed and consequently minor wall-thickness variation. So, because of relaxation pause after plug-assist stage and also implementation of two stage thermoforming process have minor wall-thickness variation and frozen-stresses and consequently better mechanical properties of thermoformed articles.

## CONCLUSION

Since wall-thickness variation has a direct effect on mechanical properties of polymeric products such as strength and toughness, so a method for having minimum wall-thickness variation is developed. Because of implementation of two-stage combinational thermoforming process and also relaxation pause after plug-assist stage has been observed minor wall-thickness variation and consequently better mechanical properties of thermoformed article. It is well known that the stage of vacuum-forming with a pre-stretched sheet occurs too quickly for experiencing of relaxation processes in the polymeric sheet. This will result in this fact that almost all accumulated deformations in polymeric sheet within this stage are elastic. In contrast to the second stage, the stage of plug-assisted can be regulated in the sense that it is technically possible to control the motion of the plug. This creates a practical opportunity that at this stage to organize the relaxation process of elastic deformations

accumulated in a polymeric sheet during the process of plug-assist forming. By using of presented model in this paper it is not only possible to estimate wall-thickness distribution of product but also evaluate the kinetics of thermoforming process such as stress and strain.

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