Rheological Modeling for Shape-Memory Thermoplastic Polymers

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Abstract—This paper presents a rheological model for producing shape-memory thermoplastic polymers. Shape-memory occurs as a result of internal rearrangement of the structural elements of a polymer. A non-linear viscoelastic model was developed that allows qualitative and quantitative prediction of the stress-strain behavior of shape-memory polymers during heating. This research was done to develop a technique to determine the maximum possible change in size of shape-memory products during heating. The rheological model used in this work was particularly suitable for defining process parameters and constructive parameters of the processing equipment.

Keywords—Elastic deformation, heating, shape-memory polymers, stress-strain behavior.

I. INTRODUCTION

SHAPE-MEMORY occurs as a result of internal rearrangement of the structural elements of a polymer. The ability of a polymer to shrink when it is subjected to heat is due to elastic deformation of the polymer [1], [2]. Heat-shrinkable polymeric articles have wide-ranging industrial application such as in heat-shrinkable tubing, packaging industry, insulating wires, provision of abrasion resistance and environmental protection for stranded and solid wire conductors, connections and joints and terminals in electrical engineering. Heat shrinking can also be used to repair the insulation on wire or to form bundles of wires, to protect wires or small parts from minor abrasion and to create cable entry seals for environmental protection [3]-[6].

Existing multi-stage manufacturing technology of polymeric heat-shrinkable products requires several steps and uses specialist kinds of equipment.

The basic technological procedure for manufacturing heat shrinkable products is as follows:
- In the first step of the production process, a tubular polymeric article is prepared by extrusion;
- In the second step, radiation exposure or chemical action is used in the resulting material to provide crosslinking of the polymer chains to form a three-dimensional polymer network structure, like the structure in vulcanized rubber, which makes it possible, with further deformation of an article, to lay in it only elastic deformation and to hinder development of viscous deformation (irreversible deformation).
- In the third step, the spatial structure is heated and then placed in a cooled inflatable mold in which compressed gas is used for inflation, wherein, due to cooling of the inflatable mold, thermo-fixing elastic deformation occurs in the product. If the blank is heated, resizing of the product will occur due to elastic deformation embedded in the polymeric product, and consequently the original size of the material is achieved.

Disadvantages of this technology are that it requires several steps, and specialist equipment and implementation of radiation exposure or chemical crosslinking of the polymer, which makes the technology low in efficiency, costly and environmentally unsafe. Furthermore, the process of shape-memory often uses the technique of applying various types of adhesive to the surface of insulated or connected products, which is undesirable because radiation or chemically modified polymers usually lose their adhesive properties. As melted polymer materials exhibit not only a viscous property but also elastic properties, this raise the following question: Is it possible when blow molding hollow tubular articles to suppress viscous properties of the deformed polymer and translate it into a state of forced elasticity?

Most of the earlier modeling research has introduced rheological models consisting of spring, dash-pot, and frictional elements in one-dimensional models, in order to quantitatively describe the shrinkage behavior in amorphous polymers. However, despite their simplicity, such models usually lead to predictions agreeing only qualitatively with experiments [2], [3]. This study was done because there is currently a lack of appropriate constitutive rheological relations for the production of hollow heat-shrinkable polymeric articles.

II. RHEOLOGICAL MODEL

To describe the stress-strain behavior of the polymeric tubular blank, inflated by compressed gas, using the following rheological model.

\[
\sigma + p\delta = 2\tau W_1 - 2\tau^{-1}W_2
\]

\[
\tau = \frac{1}{\theta} \left( \frac{\theta}{\theta} \right)^{-1} \left( \frac{\theta}{\theta} \right) \frac{\theta}{\theta} \left[ \left( \tau \frac{\theta}{\theta} \right)^{-1} \left( \tau \frac{\theta}{\theta} \right) \right] W_1 - \left( \tau \frac{\theta}{\theta} \right) \left( \tau \frac{\theta}{\theta} \right)
\]

\[
\frac{d\delta}{dt} + \tau \delta - \tau (\xi - \tau) \frac{\theta}{\theta} (\xi - \tau) = 0
\]

where \( \sigma \) is the stress tensor, \( p \) is the Lagrange multiplier,
determined by the boundary condition, \( \bar{\sigma} \) is the identity tensor, \( \bar{\tau} \) is the Cauchy strain tensor, \( \bar{\tau}_f \) is the flow strain rate tensor, \( \bar{\omega} \) is the vortex tensor, \( \bar{\sigma} \) is the strain rate tensor, \( \psi \) is dimensionless parameter (\( \psi = 0 \) at \( \omega = 0 \) and \( \psi = 1 \) at \( \bar{\omega} \neq 0 \)), \( \alpha \) is dimensionless parameter (\( \alpha = 1 \) at \( \omega 
eq 0 \) and \( \alpha = 0 \) at \( \omega = 0 \)) that characterize the presence or absence of reversible destruction of the structure of the polymer during deformation, \( \beta \) is the flexibility of macromolecular chains, \( \theta_0(\tau) \) is the relaxation time, \( G(T) \) is the tensile modulus, \( W \) is the strain energy function, \( \epsilon_{\beta} \) is the rate of deformation of the tubular blank \( \dot{I} \), \( I_1 \) and \( I_2 \) are the primary and secondary strain tensor invariants, \( t \) is the time, \( J(I_1, I_2) \) is the dimensionless function that defines relaxation time, and \( 2W^S = W(I_1, I_2) + W(I_2, I_1) \) is the symmetric function of \( W \). The strain energy function parameters can be shown by: 
\[
W_1 = \frac{\partial W}{\partial I_1}, \quad W_2 = \frac{\partial W}{\partial I_2},
\]
\[
W^S_1 = \frac{\partial W^S}{\partial I_1}, \quad W^S_2 = \frac{\partial W^S}{\partial I_2}.
\]

To describe the elastic properties of the polymer material in the rheological model (1), the following elastic potential which gives a fairly adequate results in a variety of kinematic types of polymer media under loading [2]:
\[
W = 0.25G_0(I_1 + I_2 - 6)
\]

Given the fact that during inflation of the tubular blank only increase its diameter, and its length is virtually unchanged. Due to the fact that the upper and lower ends of the blank clamped in the mold, we can assume that the deformation of the blank is carried out by mechanism of pure shear. In this case, the kinematic tensors and tensor of elastic deformation in the rheological model (1) will have the following form:
\[
\bar{\tau} = \dot{\epsilon} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \bar{\omega} = 0, \quad \bar{\sigma} = \begin{pmatrix} c & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & c^{-1} \end{pmatrix}, \quad \bar{\tau}_f = \frac{1}{\det \bar{\tau}} \begin{pmatrix} c^{-1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & c \end{pmatrix}
\]

where \( \dot{\epsilon} = \frac{1}{\lambda} \frac{d\lambda}{dt} \) is the rate of deformation of the tubular blank in its circumferential direction, \( c \equiv \lambda_c^2 \), \( \lambda_c \), \( \lambda \) are the elastic and total stretch ratio in the polymer, respectively.
\[
\lambda_c = \exp(e_c^H), \quad \lambda = \exp(e^H)
\]
where \( e^H \) is the Hencky strain, and \( e_c^H \) is the elastic Hencky strain.

The primary and secondary invariants of tensor \( C \) are resulted from (3) as:
\[
I_1 = I_2 = c + 1 + c^{-1}
\]

By utilizing (2), (3), and (4), the following form of (1) can be developed.
\[
\pi + \rho - \frac{\beta}{G(T)} = \begin{pmatrix} c - c^{-1} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & c^{-1} - c \end{pmatrix}
\]

\[
e_j = \frac{d\epsilon_j}{dt} = \frac{1}{4\theta_0(T)} \exp[-\beta(c + c^{-1} - 2)] \begin{pmatrix} c - c^{-1} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & c^{-1} - c \end{pmatrix}
\]

\[
\frac{d\pi}{dt} = 2\epsilon_\tau - \epsilon_\tau^H
\]

where \( \epsilon_\tau^H \) is the flow strain tensor as defined in Hencky.

III. RESULTS AND DISCUSSION

Now, if we can find a solution to the latter tensor equation, it will be possible to obtain dependence describing the development of elastic deformation of the material, the analysis of which can be used to assess the possibility of transferring a polymer material to a state of "forced" elasticity, whereby it will develop only elastic deformation. The following physical considerations were used to solve the problem.

Firstly, it was noted that the normal stresses acting on the thickness of a deformable blank can be neglected because of the small gas overpressure that is installed in the cavity of the inflated blank [2]. This makes it possible from (5), to determine expression for the Lagrange multiplier:
\[
P = 0.5G_0(T)(c^{-1} - c)
\]

Secondly, by taking into account that the stretch ratio is defined as \( \lambda = r(t)/r_0 \), the rate of deformation can be determined from (3) as:
\[
\dot{\epsilon} = \frac{1}{\lambda} \frac{d\lambda}{dt} = \frac{1}{r(t)} \frac{dr(t)}{dt}
\]

Relationship between the dimensionless current radius of the deformable blank \( r(t)/r_0 \) and the process parameters of inflating will be as:
\[
r(t) = r_0 \left[ 1 + \frac{(P_0 + AP)}{P_0} \right]^{\frac{1}{2}} G_v V_0 t
\]

where \( P_0 \) is the initial gas pressure within the blank, \( P_s \) is gas pressure, \( AP \) is gas overpressure in cavity of blank, \( V_0 \) is the
volume of the cavity of initial tubular blank, $k$ is the adiabatic sign of the blowing gas.

The value of the volumetric flow rate of gas ($G_n$) through an inflatable nipple can be determined from:

$$G_n = \mu_p S_n \sqrt{\frac{2k}{k-1} R_p T_p}$$  \hspace{1cm} (11)

where $\mu_p$ is the coefficient of pneumatic consumption, providing a supply of pressurized gas from the receiver, $S_n$ is the cross sectional area of openings of nipple, $R_p$ and $T_p$ are the universal gas constant and temperature of the compressed gas in the receiver, respectively.

Considering (10) and (11) the rate of deformation of the inflated blank is determined as:

$$\dot{\varepsilon}(t) = \frac{\dot{\varepsilon}(0)}{1 + 2\dot{\varepsilon}(0) \theta}$$  \hspace{1cm} (12)

Expression (12) allows determination of the values of all components included in the first equation of the kinematic tensors (3). Now, using this tensor and (6) and (7) the following scalar differential equation can be obtained that describes kinetics of the process of elastic deformation in the material in its circumferential direction:

$$\frac{dc}{dt} = 2c \left[ \frac{E(0)}{1 + 2E(0) \theta} - \frac{(c-c^*)}{4} \exp \left[ -\beta \left( c + c^* - 2 \right) \right] \right]$$  \hspace{1cm} (13)

where $\tilde{t} = \frac{t}{\Theta(T)}$ is dimensionless time, and $E(0) = \dot{\varepsilon}(0) \cdot \Theta(\Theta)$.

Since, in initial extruded tubular blanks, any missing deformation including elastic deformation allows formulation of the following initial conditions for solutions of (13):

$$C = 1$$  \hspace{1cm} (14)

Solution of (13) with initial condition (14) for different values of the dimensionless parameter of $E(0)$ is presented in Fig. 1.

Analysis of solutions of (13) is confirmed by the experimental data, the comparison of which is represented in Fig. 1. Fig. 1 shows that under certain conditions the deformation process of polymeric material goes into a state of "forced" elasticity and practically ceases to flow, like a deformed elastic medium. Data presented in Fig. 1 clearly demonstrates realization modes corresponding to curves 1 and 2 and that elastic deformation of the material was developed only in the initial moment of deformation of the blank, and then it relaxed to zero. Implementation of the same modes corresponding to curves 3 and 4 shows that elastic deformation of the material developed during the deformation time, and reached hundreds of percent or more. These results indicate that under practical conditions, the level of accumulated elastic deformation can be determined by dimensionless initial rate of deformation of the material, $E(0)$.

Consequently, for the production of heat-shrinkable articles from conventional unmodified polymer, it is necessary that the initial rate of deformation exceeds a certain critical value, which is formalized as the following conditions:

$$E(0) \equiv \dot{\varepsilon}(\tau = 0) \cdot \Theta(T) E_{cr}$$  \hspace{1cm} (15)

where $E(0)$ is the initial rate of deformation, and $E_{cr}$ is the critical value of rate of deformation.

Unfortunately, it is impossible to estimate theoretically the critical value of this quantity, however, based on analysis of (13), it is definitely determined by the dimensionless rheological parameter that characterizes rigidity of the polymer chain ($\beta$). In rigid polymers ($\beta \approx 0$), there is a lower rate of accumulation of elastic deformation compared to the rate of a relaxation process. Consequently, accumulation of elastic deformation in these polymers requires a high rate of deformation. However, with known values for rheological parameters of the polymer ($\beta, \Theta(T)$) and use of (13), varying the latter value $E(0)$, it is possible to establish a critical value of the dimensionless initial rate of deformation for each case, so in practice the desired result can be achieved. Fig. 1 shows heat-shrinkable coupling from a conventional unmodified polymer obtained by one-step technology of extrusion-blow molding and various examples of its practical application. One of the main technical characteristics of heat shrinkable products is that its value quantifies the maximum possible change in size when it is heated.
IV. CONCLUSION

From this paper it is obvious that identically sized heat shrinkable products may have completely different shape-memory characteristics that will define the value accumulated in the polymer material at the end of the formation process $c(t = t_f)$. According to (12), (13) and data presented in Fig. 1, the value of $c(t = t_f)$ depends not only on rheological parameters of the polymer and technical parameters of blow-molding process, but also on some of the constructive parameters of the equipment. A successful one-step production technology of heat shrinkable products from conventional non-modified thermoplastic polymeric materials has been reported.

REFERENCES