Mathematical Modeling for Heat-Shrinkable Polymeric Article Production

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***Abstract*— This paper presents a rheological model for producing hollow heat-shrinkable polymeric articles from thermoplastic materials. Heat-shrinking occurs as a result of internal rearrangement of the structural elements of a polymer. Practical tests for a one-step production technology of heat shrinkable products from conventional non-modified thermoplastic polymeric materials were successful. A non-linear viscoelastic model was developed that allows qualitative and quantitative prediction of the stress-strain behavior of heat-shrinkable polymers during heating and stretching. This research was done to develop a technique to determine the maximum possible change in size of heat-shrinkable products during heating. The rheological model used in this work was particularly suitable for defining process parameters and constructive parameters of the processing equipment and it provided a one-step production process for heat shrinkable thermoplastic articles.**

***Keywords*—mathematical modeling; rheology; heat-shrinkable polymers; stress-strain behavior**

I. INTRODUCTION

Heat-shrinking 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 [5-6].

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 heat-shrinking 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 raises 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 [5]?

In this state, it will grow almost exclusively elastic (rubbery) deformation during deformation of the polymer, which is then frozen by cooling the molded article in the inflatable mold; its material structure remains, thus facilitating heat-shrinkability. Further heating of the product with the oriented macromolecular structure will cause shrinkage due to relaxation of the accumulated elastic deformations. If this technology for producing heat shrinkable products, in one step by extrusion blow molding is fundamentally feasible, then it will be confirmed by the process described in Fig. 1.

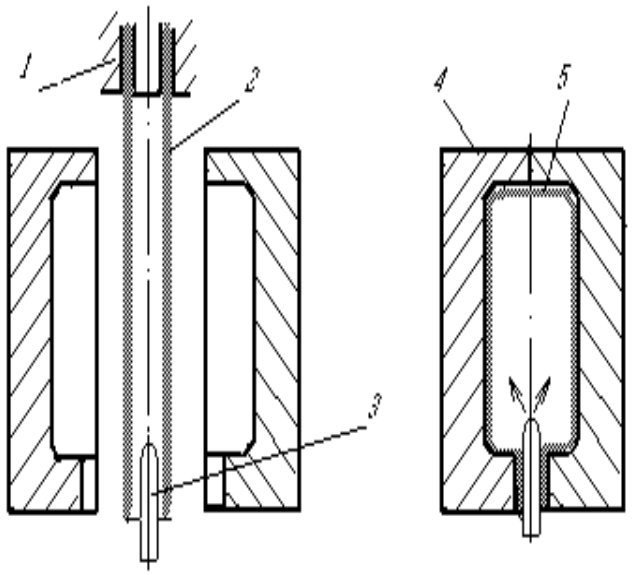

Fig.1. Scheme of extrusion-blow molding process. 1- extrusion head, 2- extrudate, 3- in-flatable nipple, 4- mold, 5- molded article.

This is a simplified process and hence the technology involved in the process becomes much cheaper for this class of product due to exclusion of radiation or chemical modification of the polymer structure and further heating and cooling of the article. In addition, the method doesn't require the use of adhesives so the product has better environmental safety. Assessment of the possibility of practical realization of such a process can be carried out on the basis of a mathematical description of the deformation behavior of the tubular extruded material from melted viscoelastic polymer when it is blow-molded into a hollow article.

Most of the earlier modeling research [5-7] 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. 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. MATHEMATICAL MODELING

To describe the stress-strain behavior of the polymeric tubular blank, inflated by compressed gas, using the following rheological model [5].

$$\begin{cases} \bar{\sigma} + p\bar{\delta} = 2\bar{c}W_1 - 2\bar{c}^{-1}W_2 \\ \bar{e}_f = \dfrac{1}{\theta_0(T)G_0(T)}\exp\left\{\alpha\psi\dfrac{I_1-3}{I_1-1} - \beta\dfrac{W^S}{G_0(T)}\right\}\left[\left(\bar{c} - \dfrac{I_1}{3}\bar{\delta}\right)W_1^S - \left(\bar{c}^{-1} - \dfrac{I_2}{3}\bar{\delta}\right)W_2^S\right] \\ \dfrac{d\bar{c}}{dt} + \bar{\omega}\bar{c} - \bar{c}\bar{\omega} - \bar{c}\left(\bar{e} - \bar{e}_f\right) - \left(\bar{e} - \bar{e}_f\right)\bar{c} = 0, \end{cases} \quad (1)$$

where $\bar{\sigma}$ is the stress tensor, p is the Lagrange multiplier, determined by the boundary condition, $\bar{\delta}$ is the identity tensor, $\bar{c}$ is the Cauchy strain tensor, $\bar{e}_f$ is the flow strain rate tensor, $\bar{\omega}$ is the vortex tensor, $\bar{e}$ is the strain rate tensor, ψ is dimensionless parameter (ψ =0 at $\bar{\omega}$ =0 and ψ =1 at $\bar{\omega} \neq 0$), α is dimensionless parameter (α = 1 at $\omega \neq 0$ and α = 0 at $\omega = 0$) that characterize the presence or absence of reversible destruction of the structure of the polymer during deformation, β is the flexibility of macromolecular chains, $\theta_0(T)$ is the relaxation time , $G_0(T)$ is the tensile modulus, W is the strain energy function $W = W(I_1, I_2)$, I_1 and I_2 are the primary and the secondary strain tensor invariants, t is the time, $f(I_1, I_2)$ 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.

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 [5].

$$W = 0.25G_0(I_1 + I_2 - 6) \quad (2)$$

Given the fact that during inflation of the tubular blank only increase its diameter (Fig. 1), 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:

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

$$\bar{c}^{-1} = \frac{1}{\det\bar{c}}\begin{pmatrix} c^{-1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & c \end{pmatrix} \quad (3)$$

where $\dot{\varepsilon} \equiv \dfrac{1}{\lambda}\dfrac{d\lambda}{dt}$ is the rate of deformation of the tubular blank in its circumferential direction, $c \equiv \lambda_e^2$; λ_e, λ are the elastic and total stretch ratio in the polymer, respectively.

$\lambda_e = exp(\varepsilon_e^H)$, $\lambda = exp(\varepsilon^H)$ where ε^H is the Hencky strain, and ε_e^H is the elastic Hencky strain.

The primary and secondary invariants of tensor C are resulted from Equation (3) as:

$$I_1 = I_2 = c + 1 + c^{-1} \quad (4)$$

By utilizing Equations (2), (3), and (4), the following form of Equation (1) can be developed.

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

$$e_f \equiv \frac{d\bar{\varepsilon}_f^H}{dt} = \frac{1}{4\theta_0(T)}\exp\left[-\beta\left(c+c^{-1}-2\right)\right]\cdot\begin{pmatrix} c-c^{-1} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & c^{-1}-c \end{pmatrix} \quad (6)$$

$$\frac{d\bar{c}}{dt} = 2\bar{c}\left(\bar{e}-\bar{e}_f\right) \quad (7)$$

where $\bar{\varepsilon}_f^H$ 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 [5]. This makes it possible from Equation (5), to determine expression for the Lagrange multiplier:

$$p = 0.5G_0(T)\cdot\left(c^{-1}-c\right) \quad (8)$$

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 Equation (3) as follows:

$$\dot{\varepsilon}(t) \equiv \frac{1}{\lambda(t)}\frac{d\lambda(t)}{dt} = \frac{1}{r(t)}\frac{dr(t)}{dt} \quad (9)$$

Relationship between the dimensionless current radius of the deformable blank ($r(t)/r_0$) and the process parameters of inflating will be as follows [1]:

$$\frac{r(t)}{r_0} = \sqrt{1+\left(\frac{P_0+\Delta P}{P_u}\right)^{-1/k}\frac{G_u}{V_0}t} \quad (10)$$

where P_0 is the initial gas pressure within the blank, P_u is gas pressure, ΔP 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_u) through an inflatable nipple can be determined from the following equation [5]:

$$G_u = \mu_p S_n\sqrt{\frac{2k}{k-1}R_P T_P} \quad (11)$$

where μ_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 expressions (10) and (11) the rate of deformation of the inflated blank is determined as follows:

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

where $\dot{\varepsilon}(0) \equiv \dot{\varepsilon}(t=0) = \frac{1}{2}\left(\frac{P_0}{P_u}\right)^{-1/k}\frac{G_u}{V_0}$.

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 Equations (6-7) the following scalar differential equation can be obtained that describes kinetics of the process of elastic deformation in the material in its circumferential direction:

$$\frac{dc}{d\tilde{t}} = 2c\left\{\frac{E(0)}{1+2E(0)\tilde{t}} - \frac{\left(c-c^{-1}\right)}{4}\cdot\exp\left[-\beta\cdot\left(c+c^{-1}-2\right)\right]\right\} \quad (13)$$

where $\tilde{t} \equiv \frac{t}{\theta_0(T)}$ is dimensionless time, and $E(0) = \dot{\varepsilon}(0)\cdot\theta_0(T)$.

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

$$\text{at } \tilde{t} = 0 \quad \Longrightarrow \quad c \equiv 1 \quad (14)$$

Solution of Equation (13) with initial condition (14) for different values of the dimensionless parameter of $E(0)$ is presented in Fig.2.

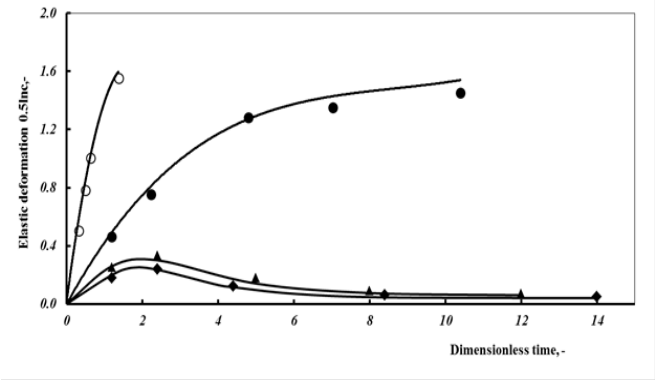

Fig.2. The kinetics of elastic deformations of LDPE in the inflated tubular blank at various modes of its deformation: ■ - E(0)=0.41; ▲ - E(0)=0.6; ● -

E(0)=1.25; ○ - E(0)=8.6; points: experimental data; curves: theoretical model; rheological parameters: β=0.38 and θ0=0.05 sec; T=423K.

Analysis of solutions of Equation (13) is confirmed by the experimental data, the comparison of which is represented in Fig.2. Fig. 2 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. 2 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:

$$E(0) \equiv \dot{\varepsilon}(\tau = 0) \cdot \theta_0 \rangle E_{cr} \qquad (15)$$

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 the differential equation (13), it is definitely determined by the dimensionless rheological parameter that characterizes rigidity of the polymer chain (β). 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 ($\beta, \theta_0(T)$) and use of the differential equation (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.4 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.

Fig.3. A heat-shrinkable coupling (left) of a conventional non-modified polymer and examples of its practical application as: element of the connection portions of the glass pipeline; sheeting weld metal pipeline; protective coating portion of the metal pipeline.

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. This characteristic is called the coefficient of heat-shrinking and is defined as follows:

$$K_{hs} = \frac{\lambda_e - 1}{\lambda} \qquad (16)$$

where λ is the stretch ratio of initial tubular blank during blow-molding, and λ_e is the elastic stretch ratio.

If the known diameter of the initial tubular blank (d_i), from which an inflated, heat-shrinkable article is produced with diameter (D_a), then the stretching ratio can be easily determined as follows:

$$\lambda = \frac{D_a}{d_i} \qquad (17)$$

Since, in accordance with $\lambda_e \equiv \sqrt{c}$, elastic component of the stretch ratio is determined by solution of the differential equation (13) with the initial conditions (14). The different values of the dimensionless parameter of the process (*E(0)*) will provide a variety of finite values of elastic deformation that determine the value of the final dimensionless molding time. As shown in [1], the final dimensionless molding time is defined as follows:

$$\tilde{t}_\phi = \frac{(V_\phi - V_0)}{\theta_0(T) G_u} \left(\frac{P_0}{P_u} \right)^{1/k} \qquad (18)$$

Where $V_\phi and V_0$ are the volume of the cavity of molding tool and volume of the initial tubular blank, respectively.

Thus, taking into account Equations (17,18), the coefficient of heat-shrinking can be determined for a particular product from Equation (16) as follows:

$$K_{hs} = \frac{d_i}{D_a}\left(\sqrt{c(\tilde{t} = \tilde{t}_{\Phi}) - 1}\right) \quad (19)$$

where $c(\tilde{t} = \tilde{t}_{\Phi})$ is determined by the solution of the differential equation (13) with initial conditions (14).

IV. CONCLUSION

From Equation (19) it is obvious that identically sized heat shrinkable products may have completely different heat-shrinking characteristics that will define the value accumulated in the polymer material at the end of the formation process . According to Equations (12,13) and data presented in Fig. 2, the value of 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 poly-meric materials has been reported. These results demonstrate that for the practical implemen-tation of the one-step production technology of heat shrinkable products, we can use well-known equipment commonly used for the extrusion blow-molding of hollow articles subject to adjustment of certain technological parameters of the formation process.

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