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Effect of Rheological Parameters on Curing Rate during NBR Injection Molding

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Abstract. In this work, non-isothermal injection molding process for NBR rubber mixture considering Isayev–Deng curing kinetic model, generalized Newtonian model with Carreau-WLF viscosity was modeled by using finite element method in order to understand the effect of volume flow rate, index of non-Newtonian behavior and relaxation time on the temperature profile and curing rate. It was found that for specific geometry and processing conditions, increase in relaxation time or in the index of non-Newtonian behavior increases the curing rate due to viscous dissipation taking place at the flow domain walls.

Keywords: Injection molding, Rubber, Computational analysis, Mold.

PACS: 83.50.Uv, 81.05.Lg, 46.15.-x, 83.10.Rs, 83.50.Ax, 66.20.-d

INTRODUCTION

Rubber injection molding of rubber began in the early 1940s. Today, the process is used for manufacturing a wide range of industrial products.

Injection molding of rubber is a process whereby a rubber mixture is injected into a closed mold where the material is shaped to the desired geometry. The material parameters that define the mold-filling process are based on the thermal and rheological properties.

When the cavity is filled, temperature gradients persist in the rubber. With having completely filled the cavity rubber mixture is vulcanized. Vulcanization is the process whereby a viscous and tacky uncured rubber is converted into an elastic material through the incorporation of chemical crosslinks between the polymer chains. The degree of cure achieved depends on the following main parameters:

- the temperature of the material when the mold is completely filled;
- the temperature of the mold cavity;
- the time for which the material is kept in the mold, that is, the cure time.

In this work, non-isothermal injection molding process for rubber mixture considering Isayev–Deng curing kinetic model, generalized Newtonian model with Carreau-WLF viscosity was modeled by using Finite Element Method (FEM) in order to understand the effect of volume flow rate, index of non-Newtonian behavior and relaxation time on the temperature profile and curing rate. For such purpose, commercially available Cadmould 3D-F software was used.

THEORETICAL ANALYSIS

Materials, Viscosity and Curing Model

In this work, two groups of virtual materials were created from the reference NBR material taken from the Cadmould 3D-F software database by changing index of non-Newtonian behavior/relaxation time by keeping the remaining parameters the same in the Carreau-WLF viscosity model [1,2], which is given by Eqs. 1-2.

$$\eta(\dot{\gamma}, T) = \frac{\eta_0 a_T}{(1 + \lambda a_T \dot{\gamma})^{1-n}} \quad (1)$$

$$a_T = 10^{\left(\frac{8.86|T_0 - T_s|}{101.6 + T_0 - T_s} - \frac{8.86|T - T_s|}{101.6 + T - T_s} \right)} \quad (2)$$

where η_0 is the zero shear viscosity, λ is the relaxation time, n is the index of non-Newtonian behavior and a_T is the temperature shift factor, T_0 is the reference temperature and T_s is the material constant. Degree of cure (α), representing the extent of reaction, for all considered virtual NBR materials was predicted by Isayev–Deng model [2,3] as follows:

$$\alpha = \frac{K(t - t_i)^{n_1}}{1 + K(t - t_i)^{n_1}} \quad (3)$$

where K and n_1 are kinetic constant and order of reaction, respectively. During the induction period (t_i) the curing reaction does not take place. This parameter is considered to be temperature dependent by an Arrhenius-type equation:

$$t_i = t_0 \exp\left(\frac{T_0}{T}\right) \quad (4)$$

where t_0 and T_0 are material constants. K parameter in Eq. 3 represents a rate constant with an Arrhenius-type dependence:

$$K = K_0 e^{\left(\frac{E}{RT}\right)} \quad (5)$$

where K_0 is a material constant, E is the activation energy and R is the gas constant.

Carreau-WLF and Isayev–Deng model parameters for all eight virtual NBR materials are provided in Table 1.

TABLE 1. Carreau-WLF and Isayev–Deng model parameters for all eight virtual NBR materials.

Carreau-WLF viscosity model		Isayev–Deng curing model	
η_0 (Pa.s)	16486.1304	t_0 (min)	$10^{-4.5290}$
λ (s)	100; 10; 1; 0.01	T_0 (K)	5273.2208
n	1; 0.7; 0.5; 0.2	K_0 (min^{-n_1})	$10^{20.0340}$
T_0 ($^{\circ}\text{C}$)	90	E_0 ($\text{kJ}\cdot\text{mol}^{-1}$)	168.6758
T_s ($^{\circ}\text{C}$)	-88.44	n_1	2.8283

Injection Molding Flow Domain

Model of two cavity product was made for computational analysis. It consists of sprue, 100 mm long runner with circular section and cube cavity which has 30x30x30 mm dimension.

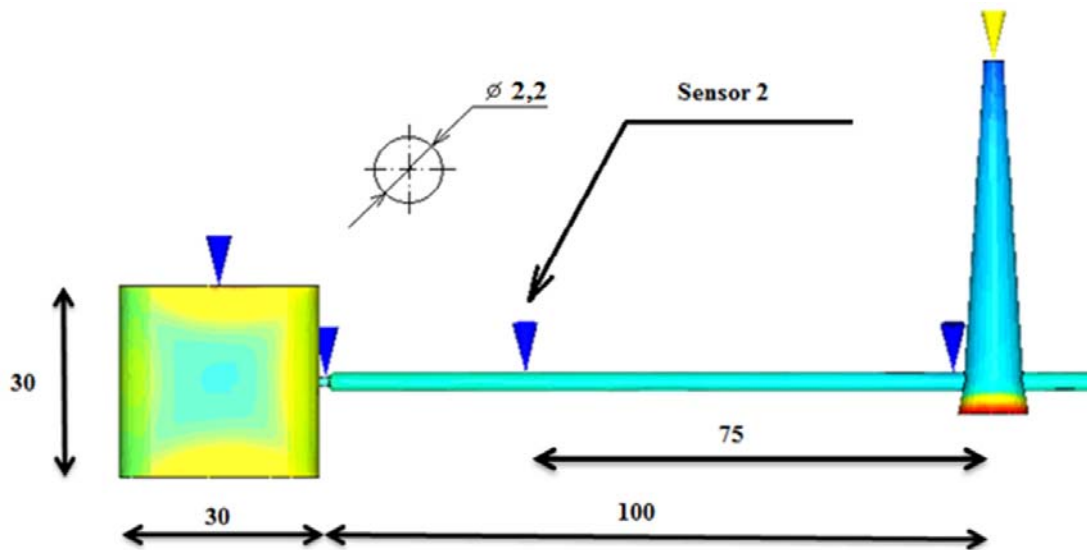


FIGURE 1. Analyzed flow domain of two cavity product. Length of channel is 100 mm. Results were received from sensor 2.

Computational Details

The computations were performed on Intel(R) Core (TM) QUAD CPU Q 6600 @ 2.40 GHz, 2 GB RAM memory, 64 – bit operation system. Part model was covered by computational mesh where element edge length was 1.5 mm. Typical calculation time was about 35 minutes. Process parameters utilized in the theoretical analysis were kept the constant (see Table 3) at two different volume flow rates whereas index of non-Newtonian behavior, n , or relaxation time, λ , in Carreau-WLF model were systematically varied.

TABLE 2. Process parameters.

	NBR
Flow rate ($\text{cm}^3 \cdot \text{s}^{-1}$)	0.7; 7.6
Pressure – controlled filling (%)	99
Mass Temperature ($^{\circ}\text{C}$)	100
Wall Temperature ($^{\circ}\text{C}$)	170
Heating (s)	600
Post-Curing (s)	200

RESULTS

Temperature profiles for different n and λ values taken from sensor 2 (see Figure 1) are depicted in Figures 2-3 for the highest considered volume flow rate, $7.6 \text{ cm}^3 \cdot \text{s}^{-1}$. It is clearly visible that for given range of n (0.7-1) and λ (>10 s), chosen processing conditions and flow domain, the temperature rise takes place at the die wall where the shear rate is the highest due to the viscous dissipation, which increases the curing rate as visible from the time dependent % cure degree in Figure 4, especially at high volume flow rate. Even if the differences in time (roughly between 400-450 s) to reach 90% of cure degree are small for both volume flow rates and all utilized virtual NBR materials (see Table 3), differences in cure degree between the virtual NBR samples at short times (250-350 s) can reach more than 10%. Considering local maxima in the temperature profile at the die wall (see Figure 2-3) and the different curing history due to high values of n and λ suggests that inhomogeneous cross linking process can take place, which can negatively influence final properties of the vulcanized NBR rubber.

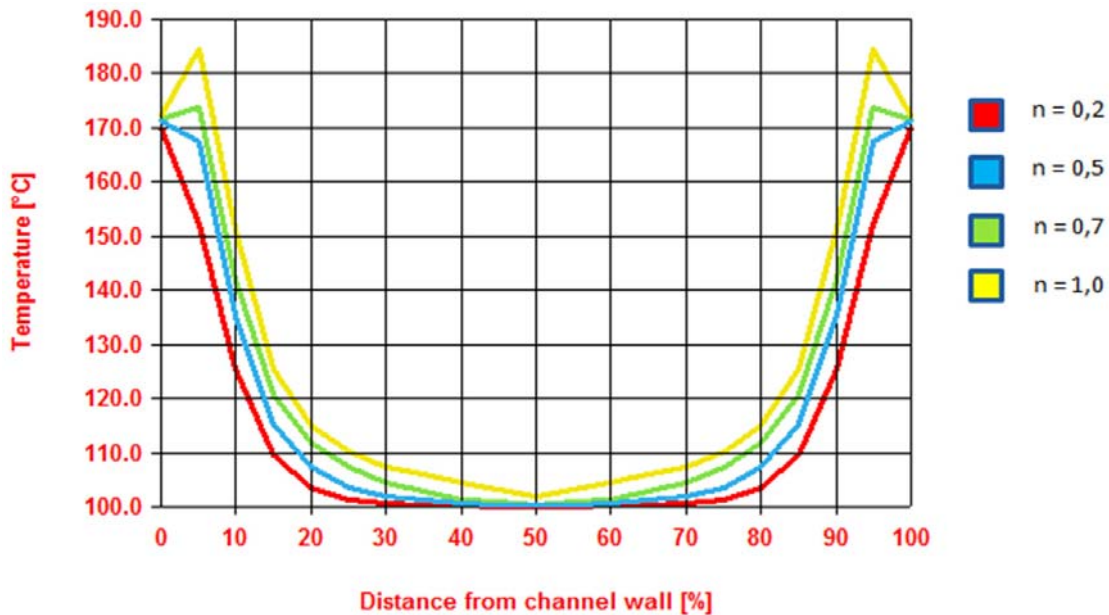


FIGURE 2. The effect of index of non-Newtonian behavior on temperature profile across the flow channel (sensor 2 location in Figure 1), volume flow rate equal to $7.6 \text{ cm}^3 \cdot \text{s}^{-1}$.

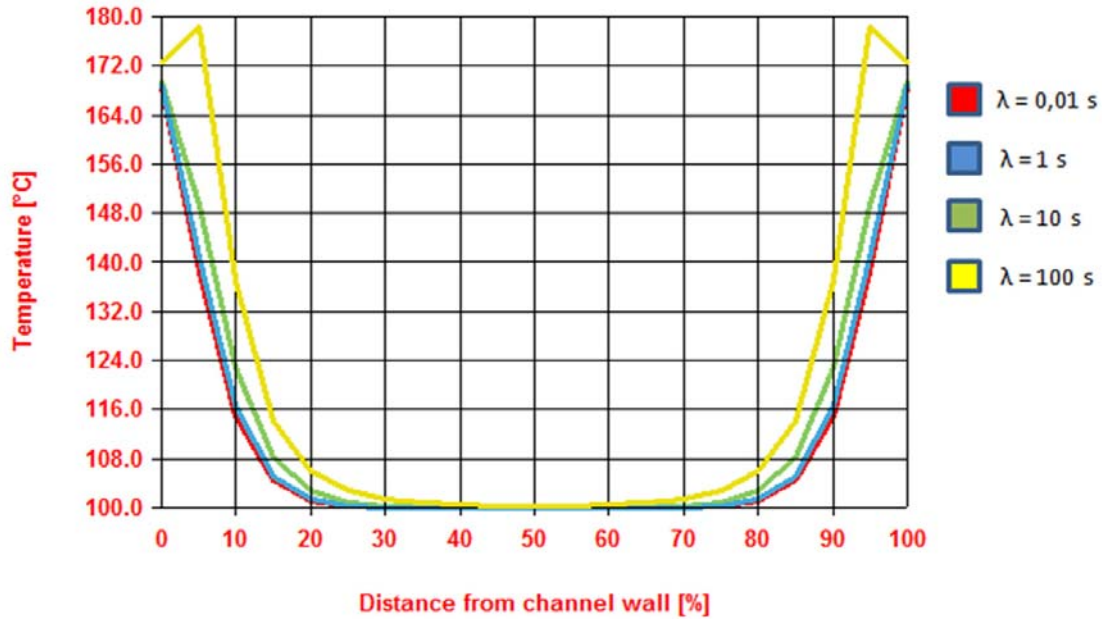


FIGURE 3. The effect of relaxation time on temperature profile across the flow channel (sensor 2 location in Figure 1), volume flow rate equal to $7.6 \text{ cm}^3 \cdot \text{s}^{-1}$.

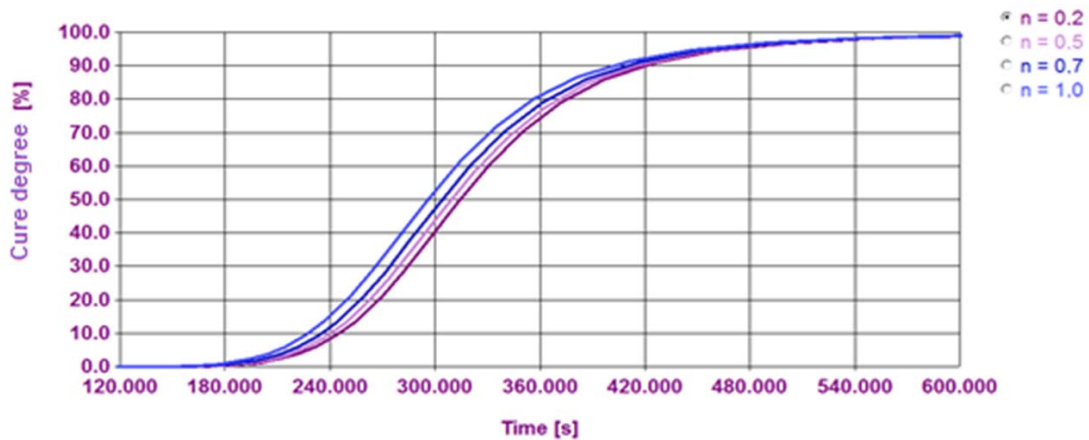


FIGURE 4. The effect of index of non-Newtonian behavior on cure degree (expressed in %), volume flow rate equal to $7.6 \text{ cm}^3 \cdot \text{s}^{-1}$.

TABLE 3. Time to reach 90% of cure degree for different flow rates and rheological parameters.

	$0.7 \text{ cm}^3 \cdot \text{s}^{-1}$	$7.6 \text{ cm}^3 \cdot \text{s}^{-1}$		$0.7 \text{ cm}^3 \cdot \text{s}^{-1}$	$7.6 \text{ cm}^3 \cdot \text{s}^{-1}$
$n = 0,2$	440.1 s	420.5 s	$\lambda = 100$	439.4 s	415.0 s
$n = 0,5$	440.0 s	414.6 s	$\lambda = 10$	438.3 s	420.7 s
$n = 0,7$	439.2 s	410.3 s	$\lambda = 1$	435.1 s	425.1 s
$n = 1$	438.8 s	402.8 s	$\lambda = 0.01$	434.9 s	425.8 s

CONCLUSION

In this work, non-isothermal injection molding process for NBR rubber mixture considering Isayev–Deng curing kinetic model, generalized Newtonian model with Carreau-WLF viscosity was modeled by using finite element method in order to understand the effect of volume flow rate, index of non-Newtonian behavior and relaxation time on the temperature profile and curing rate. It was found that for given range of n (0.7-1) and λ (>10 s), chosen processing conditions and flow domain, the temperature rise takes place at the die wall where the shear rate is the highest due the viscous dissipation, which increase the curing rate. Considering local maxima in the temperature profile at the die wall and the different curing history due to high values of n and λ suggests that inhomogeneous cross linking process could takes the place, which can negatively influence final properties of the vulcanized NBR rubber.

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