



## A study of heat transfer during molding of elastomers

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### ABSTRACT

Heat transfer is often of a great importance in several elastomer processing unit operations and even more so in the case of any variety of vulcanization process although it is seldom treated equally important as the cross-linking kinetics. Heat transfer in several elastomers was studied on a pilot scale mold utilizing various expressions for description of temperature dependent elastomer densities, heat capacities and thermal conductivities, which were applied in the governing heat equation. The latter was solved by means of quasi-exact and explicit finite difference algorithms. Molding experiments were performed for natural rubber, polybutadiene, hydrogenated butadiene–acrylonitrile copolymer, polychloroprene and polyisoprene. Whereas the molding experiments were applied for determination of the temperature dependent thermal conductivities, the temperature dependent densities and heat capacities were determined separately using pycnometry and differential dynamic calorimetry, respectively. The experimental and the predicted temperatures were in good agreement throughout the entire examined temperature range between 20 and 200 °C. Moreover, the determined parameters of the temperature dependent thermodynamic quantities may be correlated to the parameters of other, non-elastomeric polymers. The developed model along with its determined parameters may be readily applied for a wide range of elastomers and processing operating conditions or even combined with other aspects of a certain operation, such as kinetics or mechanics.

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### 1. Introduction

Heat transfer is of major importance in several polymer applications such as injection stretch-blow molding of polyethylene terephthalate bottles (Yang et al., 2004), cost-effective recovery of waste rubber from discarded tires (Agrawal et al., 2000; Wang et al., 2004), industrial applications of elastomer/filler systems (Burlett, 2004), elastomer/ceramic composites for high temperature applications (El-Tantawy, 2002), applications involving polymer blends with tailor-made properties (Chattopadhyay, 2000) and several others. Understanding of heat conduction in elastomers enables us to reduce the time involved in the design of new products and to propose technological solutions for the manufacturing process, in which all parameters should be determined in order to approach optimal conditions including reduced costs.

The superior properties and relatively low cost of several elastomers account for their use in a variety of applications. However, there are several drawbacks to the potential use of elastomers as lean materials in the uncured state like softening at higher temperatures and highly increased rigidity at lower. Therefore, the formation of network structure is one of the essential conditions for generating

the elastomeric properties. Sulfur vulcanization is the most widely used curing technique for elastomers, preferably for the unsaturated ones. The other curing methods include peroxide, resin, moisture, urethane, metal oxide and radiation cross-linking. The cross-linking is ordinarily achieved by the process of vulcanization in a mold, where heat conduction plays a determining role in defining the ultimate properties of the surface and the bulk phase of the elastomer. This is why, among all other applications, heat transfer in a vulcanization mold was studied the most extensively, usually alongside with the cross-linking process.

The distribution of state of cure in a molded elastomer component is usually non-uniform due to the slow heat transfer process involved in the molding–cooling cycle. Warley (2006) studied the effect of preheat temperature on the location of the minimum state of cure in a molded component. Numerous authors studied the heat transfer in a mold itself, while others traced the course of the process in laboratory rheometers, where the role of the heat transfer is reduced, however, not negligible. The approach to heat transfer in both cases may vary, since the low thermal diffusivity of elastomers and time-varying operating conditions cause every individual point inside the compound to have a unique history of temperature during the curing cycle. The impact of this fact is more crucial for the case of heat transfer on a larger scale. Among the authors, who studied the heat transfer in a mold, are Ghoreishy and Naderi (2005), Marzocca (1991) and Tong and Yan (2003), who studied the heat transfer

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during curing of the elastomer compound. Azaar et al. (2003) investigated the heat transfer in ethylene propylene diene elastomer discs, Calabrese and Valenza (2003) in epoxy resin modified with carboxylated nitrile butadiene elastomer, Jia et al. (2003) in silicone elastomer and Jönsson and Flodin (1991) in styrene butadiene elastomer. On the other hand, there are the authors, who considered the heat transfer during cure in laboratory scale rheometers. Rheometers are usually run under isothermal conditions throughout the elastomer cure process. Nevertheless, it takes some time for the thermal equilibrium to be reached between the elastomer sample, which is initially at room temperature, and the dies. Rosca and Vergnaud (2001) and Rosca et al. (2004a, b) examined the effect of heating rate and rubber–die contact on the vulcanization of natural rubber (NR) and ethylene propylene diene elastomer. Deiber et al. (1995) modeled the heat transfer during vulcanization of styrene butadiene and nitrile butadiene elastomer in an oscillating bicone cell.

Heat transfer in elastomers is naturally dependant on the thermodynamic properties of the latter such as density, heat capacity and thermal conductivity. In the mentioned studies of the heat transfer in elastomers either some (Deiber et al., 1995; Ghoreishy and Naderi, 2005; Marzocca, 1991) or all (Azaar et al., 2003; Calabrese and Valenza, 2003; Jia et al., 2003; Jönsson and Flodin, 1991; Rosca and Vergnaud, 2001; Rosca et al., 2004a, b; Warley, 2006) properties are considered constant or their dependence on temperature is oversimplified (Tong and Yan, 2003). This is often done owing to the fact that the heat transfer was in many cases considered of a minor importance in comparison to the complex kinetics of cross-linking, or the temperature dependence of the properties was considered negligible. This assumption is valid if the span of temperature is narrow enough, though during vulcanization the compounds are often subjected to highly increased temperature resulting in great temperature gradients within the bulk phase of the elastomer. Thermodynamic properties influencing the heat transfer and cross-linking should therefore best be studied separately to minimize the error in determining the properties and consider them in the temperature dependent form during cross-linking studies.

In order to successfully study the heat transfer in elastomers, the thermodynamic properties should be predicted or determined. There are several models for the prediction of heat capacity, such as the polymer chain-of-rotators equation of state. Its parameters were reported by Sy-Siong-Kiao et al. (1996). Further examples are the Sanchez–Lacombe (Sanchez and Lacombe, 1977) and the Flory–Orwoll–Vrij (Flory et al., 1964) equations of state, where the parameters of the latter two were reported by Rodgers (1993). The perturbed hard-sphere chain equation of state was derived by combining a modified Chiew (Chiew, 1990) equation of state for hard-sphere chains with the van der Waals attractive perturbation term by Song et al. (1994). Nevertheless, Novenario et al. (1998) compared these models with the Van Krevelen's empirical correlation (Van Krevelen, 1990) only to find that the latter quite often grants the best agreement with experimental results. Zhong et al. (2001a, b) proposed a group contribution model for the prediction of the thermal conductivity of polymer melts and a correlation for the prediction of the thermal conductivity of amorphous polymers, while the thermal conductivity of polymers is often considered linearly dependent on the heat capacity (Godovsky, 1992).

The purpose of this work was to separately establish and describe the temperature dependence of the heat capacity and density of several elastomers. The obtained dependencies were used in the governing heat equation (GHE), which was solved applying quasi-exact and finite difference method. The solutions were compared to the experimental results and critically evaluated for different types of the proposed relationships between the thermal conductivity and temperature.

## 2. Experimental

NR used in this study was a field grade Standard Malaysian Rubber (SMR 10), provided by Astlett Rubber, with nominal density of  $920 \text{ kg/m}^3$ , 99.0% *cis* polymer content, iodine value of 166–172 mg/100 mg, Mooney viscosity ( $ML_{1+4}$ ,  $100^\circ\text{C}$ ) of 55–67,  $\bar{M}_n$  of  $3.37 \times 10^5 \text{ g/mol}$  and  $\bar{M}_w$  of  $2.51 \times 10^6 \text{ g/mol}$ . Polybutadiene (BR) used in this study was SEETEC BR 1208, provided by SEETEC, with nominal density of  $910 \text{ kg/m}^3$ , 98.0% *cis* polymer content, iodine value of 231 mg/100 mg, Mooney viscosity ( $ML_{1+4}$ ,  $100^\circ\text{C}$ ) of 45,  $\bar{M}_n$  of  $1.30 \times 10^5 \text{ g/mol}$  and  $\bar{M}_w$  of  $6.17 \times 10^5 \text{ g/mol}$ . Hydrogenated butadiene–acrylonitrile copolymer (HNBR) used in this study was Zetpol 2020L, provided by Zeon Chemicals, with nominal density of  $950 \text{ kg/m}^3$ , 36.2% bound acrylonitrile, iodine value of 28 mg/100 mg (91% saturation), Mooney viscosity ( $ML_{1+4}$ ,  $100^\circ\text{C}$ ) of 58,  $\bar{M}_n$  of  $7.72 \times 10^4 \text{ g/mol}$  and  $\bar{M}_w$  of  $2.36 \times 10^5 \text{ g/mol}$ . Polychloroprene (CR) used in this study was BAYPREN 510, provided by LANXESS, with nominal density of  $1230 \text{ kg/m}^3$ , 95.9% *trans* polymer content, iodine value of 143 mg/100 mg, Mooney viscosity ( $ML_{1+4}$ ,  $100^\circ\text{C}$ ) of 42,  $\bar{M}_n$  of  $1.13 \times 10^5 \text{ g/mol}$  and  $\bar{M}_w$  of  $4.37 \times 10^5 \text{ g/mol}$ . Polyisoprene (IR) used in this study was NATSYN 2200, produced by Goodyear Chemical, with nominal density of  $920 \text{ kg/m}^3$ , 98.5% *cis* polymer content, iodine value of 185 mg/100 mg, Mooney viscosity ( $ML_{1+4}$ ,  $100^\circ\text{C}$ ) of 80,  $\bar{M}_n$  of  $3.13 \times 10^5 \text{ g/mol}$  and  $\bar{M}_w$  of  $1.02 \times 10^6 \text{ g/mol}$ . Average molecular weights were determined by gel permeation chromatography (GPC).  $\bar{M}_n$  and  $\bar{M}_w$  determination was performed using Waters 2690 (Separations Module) instrument with a refractive index detector. Three Waters Styragel columns ( $300 \text{ mm} \times 4.6 \text{ mm}$ ) were used in series. The elastomer solutions were prepared in tetrahydrofuran (THF), which was also used as a carrier solvent at a rate of 0.2 ml/min. The average molecular weights were calculated from molecular weight versus the retention time curve of polystyrene standards.

Elastomer densities were determined between 30 and  $180^\circ\text{C}$  with  $10^\circ\text{C}$  increments by the pycnometric method. Pycnometers with volumes of approximately 25 ml were used. Pycnometers' exact volumes were determined at  $25^\circ\text{C}$  using distilled water. For the purpose of measurements, 1.5–1.7 g of elastomer and suitable volume of silicone oil were prepared in the pycnometer and then settled at each temperature for 30 min before weighing.

Elastomer heat capacities were determined by differential scanning calorimetry (DSC) on DSC 821<sup>e</sup> instrument from Mettler Toledo in nitrogen atmosphere (50 ml/min). The samples were prepared by weighing 22–24 mg of elastomer in the weighted 40  $\mu\text{l}$  aluminum crucibles without pin. Samples, sapphire standard and empty crucible were subjected to heating/cooling program, presented in Fig. 1. Indium and zinc standards were applied for the temperature calibration and for the determination of the instrument time constant. Individual segments, presented in Fig. 1, served for the determination of the heat capacities of the samples. Whereas the initial dynamic segments (heating rate ranging from 10 to 50 K/min) were used for the desmearing process, the five isothermal segments during cooling (cooling rate of 10 K/min) at 0, 50, 100, 150 and  $200^\circ\text{C}$  were used for the polynomial baseline correction. The dynamic segment between  $-150$  and  $200^\circ\text{C}$  (heating rate of 10 K/min) was employed for the determination of the elastomers' phase transitions. There were isothermal gaps between the initial dynamic segments in order to stabilize the instrument's response between the individual segments.

For the purpose of heat transfer study, a pilot scale mold was constructed and is schematically presented in Fig. 2. The sides and the lid of the mold were thermally insulated in order to prevent any heat loss. As insulating material ZRCI Type RSMAT-3000 High Purity Alumina Ceramic Fiber Blanket was utilized, provided by ZIRCAR Refractory Composites, Inc., with nominal thermal conductivity of  $0.07 \text{ W/m/K}$  at  $315^\circ\text{C}$  and even lower at lower

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