Research Article

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Numerical Modeling of p-v-T Rheological Equation Coefficients for Polypropylene with Variable Chalk Content

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Abstract: The paper reports the experimental results of a study investigating the effect of different contents of a mineral filler on the rheological properties, p-v-T, of polypropylene. Using the pvT100 apparatus, we measured specific volume under isobaric cooling at different pressures for pure polypropylene and chalk-filled polypropylene (10 wt%, 20 wt% and 30 wt%). Next, we employed computer methods to determine the coefficients of a mathematical model describing the variations in specific volume in a function of temperature and pressure. The model was used in the numerical simulations of injection molding and shrinkage processes.

Keywords: numerical modelling, chalk, filler, poly(propylene), thermal properties

1 Introduction

Injection molding is the dominant method of processing polymer materials, due to the complexity of the structures of the obtained moldings (variations in shape, dimensions and mass) and the range of types of plastics that can be used. Correctly designed molding is a source of information on the basis of which the type of plastic is selected, the injection mold is constructed and the technological parameters of the injection are determined. Due to the very high

costs of starting production by injection molding, it is necessary to minimize the risk of errors at each stage of the production process preparation. Thanks to computer simulation and analysis of the results obtained, many design and technological errors can be eliminated at the design stage, thus significantly reducing costs and reducing production preparation time [2, 9].

For the proper use of injection molding programs and the correct analysis of the results obtained, it is necessary to have the necessary knowledge about rheological phenomena occurring during injection, because CAE programs used to simulate this processing method use various rheological models describing the behavior of the material under high pressure temperature. The general algorithm of simulation programs is based on solving equations of mechanics of continuous media (mass, motion, energy). Processing of polymer materials (mainly injection and extrusion) are described as three-dimensional, complex, non-Newtonian and non-isothermal flow, and sometimes as transient flow. Thus, the viscosity of polymers depends mainly on the shear rate and decreases with increasing this rate, moreover it varies depending on the temperature and pressure. The polymer viscosity decreases with increasing temperature, and increases with increasing pressure [2, 9, 17].

Numerical modeling of phenomena occurring in the injection mold during injection takes place assuming that the flow of material takes place in two dimensions, bypassing the thickness dimension. This assumption is justified by the construction of moldings, which are usually thin-walled elements, therefore the flow of material towards the thickness of the molding can be omitted [9, 17]. As a result, the equation of mass, motion and energy conservation is reduced to a locally two-dimensional problem. The equation of mass, motion and energy conservation is simplified to describe the mold filling phase and the clamping phase. In the Cadmould 3D-F program used in the research part, two rheological models are used: the Carreau model and the power model. The relationship between the viscosity of the material and temperature is described by the Williams-Landel-Ferry equation (WLF), and the relation-

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ship between the specific volume of material v and temperature T and pressure p is determined on the basis of p-v-T characteristics.

2 Thermal state of polymers

The thermal state of polymers can be described by their technical parameters such as pressure p , volume V and temperature T , as well as a physical quantity describing the amount of substance, e.g. kilomole or mass. The relation between pressure, specific volume and temperature describes a thermodynamic equation of state. The relations between the parameters of state result from the zeroth law of thermodynamics. Its general form can be expressed as the following equation [16]:

$$F(p, v, T) = 0 \quad (1)$$

where p means pressure, v denotes specific volume and T indicates temperature.

The quantities p , v and T are described as thermal parameters of the equation of state. In order to describe the thermal state of a polymer, it is enough to know two parameters of this polymer, in practice, this usually means pressure and temperature [7] which can nowadays be easily measured.

P-v-T properties are necessary, among others, in numerical simulations of injection molding processes for analysis of clamping and injection shrinkage [6, 20]. Moreover, the knowledge of p-v-T characteristics enables obtaining better results in analysis of mould cavity filling [19, 20]. P-v-T characteristics describe the relations between the specific volume v of a polymer exposed to the temperature T and the pressure p [8, 10]. The change in specific volume is simultaneously the measure of change in polymer density [4, 20]. As in the case of most substances, polymers decrease their volume during cooling and increase it when heated. Also filler content is changing of thermal properties of filler polymers [18, 21]. The change in polymer specific volume during cooling is one of the main causes of processing shrinkage [14, 22]. Changes in the shape and dimensions of a molded piece are compensated for during clamping by refilling the polymer in the injection mould [1, 19]. In the course of processing, the polymer changes from the liquid to molten state, and its rheological properties in these two states significantly differ, and thus must be described by separate equations [5].

The most popular models describing p-v-T characteristics of polymers include the Tait model and the Schmidt model (IKV). Neither of the models retains continuity

at the temperature of phase transition [3, 19]. The use of these models for numerical modeling of the injection molding process can cause problems in numerical analyses and lead to unreliability of results, e.g. when modeling variations in pressure [3]. It is assumed that the Tait and Schmidt models are sufficient to be applied both to amorphous and partly crystalline polymers [11]; however, they may turn out to be insufficient with respect to filled polymers, particularly when investigating the processing shrinkage and deformation of molded pieces. A model which offers a more detailed description of rheological properties of composite polymers is the Renner continuous model (Simcon), which has the following form [3]: for solid phase

$$v(p, T) = \alpha_s + \xi \left(\frac{T_b}{CS_5} + 1 \right) \cdot (\beta_M - \alpha_s) \quad (2)$$

for molten phase

$$v(p, T) = \alpha_M \quad (3)$$

The constants α_s , α_M , β_s , β_M and ξ describe the following relations [12]:

$$\beta_s = \frac{CS_1}{1 + CS_3 \cdot p} \quad (4)$$

$$\beta_M = \frac{CM_1}{1 + CM_3 \cdot p} \quad (5)$$

$$\alpha_s = \beta_s + \frac{CS_2 - CS_1}{1 + CS_4 \cdot p} \cdot \frac{T_b + CS_5 + 10K}{10K} \quad (6)$$

$$\alpha_M = \beta_M + \frac{CM_2 - CM_1}{1 + CM_4 \cdot p} \cdot \frac{T_b}{10K} \quad (7)$$

$$\xi = 0 \text{ for } x \leq 0; \quad (8)$$

$$\xi = CS_7 \cdot x + (1 - CS_7) \cdot x^{CS_6} \text{ for } x > 0$$

The transition temperature T_t and the fiducial temperature T_b are described by the following equations [14]:

$$T_t = CT_1 + CT_2 \cdot p \quad (9)$$

$$T_b = T - T_t \quad (10)$$

The Renner model's coefficients CS_1 , CS_2 , CS_3 , CS_4 , CS_5 , CS_6 , CS_7 , CM_1 , CM_2 , CM_3 and CM_4 as well as CT_1 and CT_2 are determined analytically based on the results of pressure p , specific volume v and temperature T [3].

3 Experimental

3.1 Materials

Test samples were produced by extrusion with pelletization on a laboratory twin-screw extruder available at a Lublin-based company, Permedia S.A. They were made of Moplen RP2380, polypropylene (random copolymer) for injection molding purposes manufactured by Lyondell Basell. The polymer has the following properties [15]: density at room temperature - 905 kg/m^3 ; melt flow index - 48 g/10min (in a temperature of 230°C under a load of 2.16 kg); tensile modulus - 1100 MPa ; yield stress - 29 MPa ; ball indentation hardness - 58 MPa ; Charpy notched impact strength (23°C) - 4.5 kJ/m^2 . The polypropylene was filled with calcium carbonate with trade name Omyacarb 2T-VA, manufactured by Omya International AG. According to the material datasheet provided by the manufacturer [13], this filler exhibits the following properties: carbonate content 98%, mean particle size $2.7 \text{ }\mu\text{m}$, packed bulk density 1300 kg/m^3 , pH value 9. The tested filler contents were: 10 wt%, 20 wt% and 30 wt%, respectively.

3.2 Experimental set-up

The investigation of the rheological properties and p-v-T characteristics of chalk-filled polypropylene was performed using the pvT 100 apparatus from SWO Polymertechnik GmbH (Germany). The apparatus consists of: a measuring system, a hydraulic system as well as a control system. The main unit of the measuring system is a cylinder in which polymer samples are placed. The cylinder is closed by the lower and upper pistons. It can generate a pressure of up to 250 MPa and can be heated to a temperature of 420°C [12]. The apparatus is part of the equipment available at the laboratory of the Department of Polymer Processing in the Mechanical Engineering Faculty at the Lublin University of Technology.

3.3 Experimental methods

According to the adopted program of experimental tests, the tested variable was mineral filler content, set to 10 wt%, 20 wt% and 30 wt% of calcium carbonate in polypropylene. The measurements were also made for pure polypropylene.

The constant factors included the parameters for determining rheological properties with the pvT100 apparatus. The p-v-T properties of composite specimens were deter-

mined by isobaric cooling. The tested temperature range was between 25°C to 240°C ; the cooling velocity was set to 2°C per minute, and the measurements were made at a temperature change set to $\Delta T = 2^\circ\text{C}$. Curves were calculated for the following values of pressure: 20 MPa , 40 MPa , 60 MPa , 80 MPa , 100 MPa and 120 MPa .

The disturbing factors included: variations in ambient temperature, humidity of the polymer, relative air humidity and variations in voltage in the mains supply. It was found that the above disturbing factors did not have a significant impact on the results.

The factors measured directly with the pvT apparatus included: pressure p , specific volume v and temperature T .

The pelletized specimens were examined with respect to their density which is one of the input data indispensable for performing analysis by the pvT 100 apparatus. The variations in density of the tested composite in a function of the applied filler content were determined by the pycnometer method. The results of the pressure p , the specific volume v and the temperature T produced by the computerized measuring system were temporarily saved as binary files, and then transformed using the “pvT-Program” software into databases for further processing. The databases obtained from the pvT 100 apparatus were processed using MS Excel spreadsheet to the CSV format which is recognized by SimFit, one of the computational modules of the Cadmould 3D-F software for numerical modeling of injection molding. The SimFit program can be used for calculating the coefficients of thermodynamic equation of polymer state. It also enables approximation of several mathematical models. As for the filler content in the polymer, the Renner continuous model of p-v-T characteristics was found to be the most adequate and thus applied.

4 Results discussion

The values of coefficients in the equation describing Renner’s continuous model depending on the content of calcium carbonate are listed in Table 1. Table 2 shows information about transition temperature versus filler content and pressure. Figures from 1 to 3 show the plots illustrating the example of p-v-T characteristics for raw polypropylene Moplen RP2380 and with 10%, 20% and 30% filler contents, respectively, obtained for selected pressure. For the purposes of clarity, Figures 1, 2 and 3 show the curves only for the selected isobars: minimum 20 MPa , medium 60 MPa and high 120 MPa .

Figure 4 presents plots illustrating p-v-T characteristics obtained with the SimFit software. The dotted lines

Table 1: Renner equation coefficients versus filler content

Filler content	Raw PP RP2380	10% of chalk	20% of chalk	30% of chalk
Solid state				
CS_1 [m ³ /kg]	0.0011238873	0,0010395317	0,00097420259	0,00090406503
CS_2 [m ³ /kg]	0.0011290388	0,0010449577	0,00097893882	0,00090815422
CS_3 [1/Pa]	3.9388653E-010	3.0128369E-10	3.8954888E-10	3.655989E-10
CS_4 [1/Pa]	2.822012E-009	5.8013513E-9	6.7413902E-9	5.0341516E-9
CS_5 [K]	76	76	58	76
CS_6 [-]	5	5,8	4	5
CS_7 [-]	0	0.05061876	0.087680517	0
Melt state				
CM_1 [m ³ /kg]	0.0012616995	0,0011688241	0,0010786346	0,0010054613
CM_2 [m ³ /kg]	0.0012713301	0,0011771861	0,00108648	0,001012326
Cm^3 [1/Pa]	7.3826347E-010	6.5475975E-10	6.8759652E-10	6.9878211E-10

Table 2: Transition temperature versus filler content and pressure

Pressure [MPa]	Filler content			
	raw PP RP2380	10%	20%	30%
Transition temperature [°C]				
20	128	132	130	130
40	132	134	134	132
60	134	138	136	134
80	136	140	138	136
100	138	142	140	136
120	140	146	140	140

Figure 1: Example of P-v-T characteristic for raw PP Moplen RP2380 and with 10%, 20%, 30% of filler content obtained at a low pressure 20MPa

mark the measuring points for individual pressures (from 20MPa to 120MPa), while the solid lines mark the curves approximated by the Renner equation. With increasing the content of the filler (calcium carbonate) in polypropylene, the specific volume v of the produced copolymer composite decreases. Between 10% and 20% of calcium carbonate,

Figure 2: Example of P-v-T characteristic for raw PP Moplen RP2380 and with 10%, 20%, 30% of filler content obtained at a medium pressure 60MPa **Figure 3:** Example of P-v-T characteristic for raw PP Moplen RP2380 and with 10%, 20%, 30% of filler content obtained at a high pressure 120MPa

the decrease in the specific volume v ranges from 7.58% to 7.81%, the effect being smaller at lower pressures (from 20MPa to 60MPa), while the highest decrease can be observed at the maximum tested pressure, i.e. 120MPa. Com-

Figure 4: Obtained p-v-T characteristic: a) raw PP RP2380, b) PP RP2380 filled with 10% of chalk, c) PP RP2380 filled with 20% of chalk, d) PP RP2380 filled with 30% of chalk; dots – measuring data, lines – numerical approximation with Renner model using SimFit software

Figure 5: Changes of specific volume depending on the pressure and the filler content at ambient temperature (25°C)

Figure 6: Changes of specific volume depending on the pressure and the filler content at processing temperature (240°C)

paring the decrease in the specific volume v at 10% and 30% filler contents, it can be observed that it is close to 13.7% when the pressure ranges from 20MPa to 100MPa, while at 120MPa it slightly increases to 13.9%. The filler content does not affect the temperature of transition from solid to melt state; with increasing the filler content the transition temperature is 402.60K, 402.62K and 402.38K, respectively.

Figure 5 presents changes of specific volume depending on the pressure and the filler content at ambient temperature (25°C) while Figure 6 presents the same dependence at processing temperature (240°C).

The obtained values of the coefficients of the thermodynamic equation of state allow us to define the polymer's rheological properties assigned in the Cadmould Material Data Base. As a result, it is possible to numerically simulate an injection molding process for such a polymer, to analyze the behavior of the polymer during injection and clamping as well as cooling of the molded part, and to determine the value of processing shrinkage and deformation of the molded piece [5]. P-v-T plots can be used to define injection parameters, from the recommended processing temperature and variations in pressure in the mould cavity, to the time of clamp and cooling of the molded

piece, such that the difference in the specific volume describing the predicted processing shrinkage is the lowest possible [3, 12].

5 Conclusions

The observed proportionate decrease in the specific volume of the tested polymer with increasing the filler content has a positive effect on the behavior of the molded piece during cooling, resulting in smaller processing shrinkage and higher dimensional accuracy. At the same time, it has been found that the injection molding process can be performed at lower pressure, which results in reduced energy consumption during processing, the use of smaller machines and lower wear of working subassemblies. The possibility of determining variations in the specific volume of the polymer in a function of pressure and temperature based on the coefficients of the thermodynamic equation of state for polymers enables determination of variations in its density under processing conditions, and – via analysis of injection shrinkage - it enables determination of the required shape and dimensions of the mould cavity in the injection mould and gates. In addition, this also helps establish the conditions of cooling for molded pieces by determining adequate times of individual stages of the injection molding process.

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