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Injection Molding Simulation with Variothermal Mold Temperature Control of Highly Filled Polyphenylene Sulfide

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Abstract. For the installation of a fuel cell stack to convert chemical energy into electricity it is common to apply bipolar plates to separate and distribute reaction gases and cooling agents. For reducing manufacturing costs of bipolar plates a fully automated injection molding process is examined. The high performance thermoplastic matrix material, polyphenylene sulfide (PPS), defies against the chemical setting and the operation temperature up to 200 °C. To adjust also high electrical and thermal conductivity, PPS is highly filled with various carbon fillers up to an amount of 65 percentage by volume. In the first step two different structural plates (one-sided) with three different gate heights and molds are designed according to the characteristics of a bipolar plate. To cope with the approach that this plate should be producible on standard injection molding machines with variothermal mold temperature control, injection molding simulation is used. Additionally, the simulation should allow to formulate a quality prediction model, which is transferrable to bipolar plates. Obviously, the basis for a precise simulation output is an accurate description of the material properties and behavior of the highly filled compound. This, the design of the structural plate and mold and the optimization via simulation is presented, as well. The influence of the injection molding process parameters, e.g. injection time, cycle times, packing pressure, mold temperature, and melt temperature on the form filling have been simulated to determine optimal process conditions. With the aid of the simulation and the variothermal mold temperature control it was possible to reduce the required melt temperature below the decomposition temperature of PPS. Thereby, hazardous decomposition products as hydrogen sulfide are obviated. Thus, the health of the processor, the longevity of the injection molding machine as well as the material and product properties can be protected.

Keywords: Polyphenylene sulfide, injection molding simulation, variothermal mold temperature control, highly filled compounds, form filling, material data
PACS: 83.50.Uv, 07.05.Tp, 81.05.Lg , 81.05.Qk, 88.30.J-, 88.30.jn 88.30.mj

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFC) already exist for many years. However, the focus and intensity of research has risen in the course of energy revolution to a regenerative hydrogen energy economy. Since high temperature PEMFC, which are able to operate at temperatures around 150-200 °C, have a wide field of application, e.g. local cogeneration, continuous power supply, backup power, mobile motor vehicles and portable devices, the development is encouraged. A large market potential is prognosticated, but can only be proven true if the performance of the PEMFC is increased and mass production enables to decrease unit costs concurrently. Therefore, injection molding of the main repetition component to assemble a PEMFC-stack, the bipolar half plate, is under investigation. The following requirements must be fulfilled by bipolar half plates: conduct electricity, dissipate heat, feed and separate process gases as well as cooling agents, mechanical stability, low-cost, reproducible in series manufacturing, resist the corrosive environment under operating temperature, temperature stability [1]. Thereby, only a few polymeric materials, especially high-performance thermoplastics as polyphenylene sulfide, can meet most of the listed demands. Ensuring an adequate conductance of electricity and heat the properties of the pure thermoplastic have to be adjusted by adding carbon based fillers as graphite, carbon black and carbon fiber. To ensure high conductivity beyond the percolation threshold the filler concentration reaches levels up to 65 percent by volume. As the addition of fillers in an upstream compounding process alter the characteristics of the pure thermoplastic drastically, especially increasing the viscosity, hence decreasing the flowability, processing agents can be used, but should be avoided as they pose a supplementary element of uncertainty.

To push the development regarding the design and layout of big bipolar plates and its appropriate mold, a preferably exact and realistic injection molding simulation is inevitable. Furthermore, the simulation should allow the prediction of critical and optimal process conditions to fill the cavity as well as shrinkage potential and welding lines. Particularly, the difficulties in material characterization as well as the different filling behavior of highly filled compounds, caused by the low melt strength leading to the absence of displacement flow as it is assumed in simulation [2], restrict the prediction accuracy of the software.

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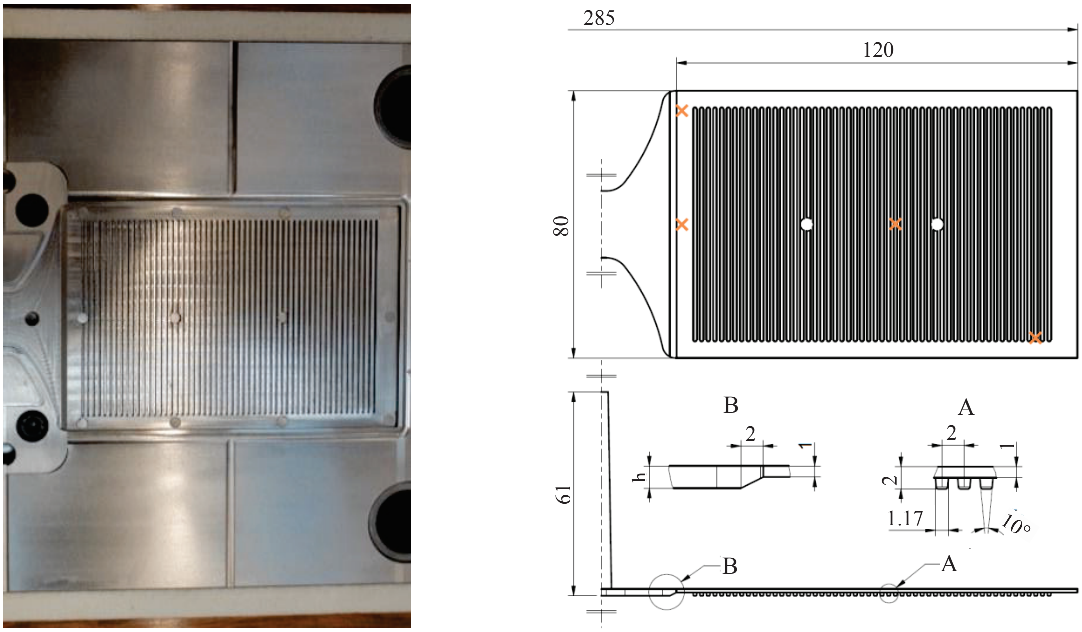
MOLD AND PART

The mold cavity is designed reconstructing the flow conditions in injection molds for bipolar half plates (refer to **FIGURE 1 (a)**). The geometry is simplified in the manner that only one side resembles the typical geometrical structure of the flow field. The film gate (with sprue) is exchangeable to analyze the influence of different designs on the electrical conductivity of the products. Draft angles and vents are considered. The whole mold is insulated to achieve low heat loss. The thermal oil, which is heated up to 350 °C, flows through two separate (cooling) circuits with diameter of 8 mm proceeding closely alongside the cavity of each mold half. The mold halves are cooled or heated separately, realizing the variothermal mold temperature control by an oil tempering device including a valve group, which permits switching between hot and cold at specific points of the injection molding cycle. The variothermal mold temperature control is necessary to achieve longer flow paths, lowering the required pressure respectively and to prohibit freezing of the material causing the formation of a skin layer of lower filler content simultaneously. The regulation of the heating/cooling unit can be realized by thermocouples (type J) or by defined time points. For form filling control cavity pressure sensors can be used at four points, as illustrated in **FIGURE 1 (b)**.



(a) (b)

FIGURE 1. (a) The movable half of the mold shows the structured side of the cavity and the exchangeable film gate. The insulation of the mold can be identified. (b) Dimensions of the cavity in mm (gate height h = 1/2/3 mm) and location of pressure sensors.

MATERIAL

A PPS grade from Celanese (Fortron 0203B6) was highly filled with graphite, carbon black, carbon fiber and processing agents. In that way the injection molding simulation is focused on a compound consisting of five material components.

The pure thermoplastic matrix material was characterized via rotational rheology (plate-plate) to build up a complete understanding of the material characteristics and to define the material properties and process limits for use in simulation software. The complex viscosity was measured at a constant angular frequency of 100 rad/s and constant deformation amplitude of 0.08 during 120 minutes. The results of the measurements at 320 °C and 340 °C under nitrogen atmosphere are shown in a double logarithmic scale in **FIGURE 2** respectively. The results indicate a low level of viscosity around 20 Pas at the start of the measurement. In the course of time the PPS starts to degrade with a marginal decrease in viscosity. After 13 minutes at 320 °C and after four minutes at 340 °C respectively a significant exponential increase of viscosity over time is detected. This measurement emphasizes the complex thermo-rheological behavior of the pure thermoplastic and the importance to comply with processing temperatures preferably below

340 °C to preserve the matrix material against damage and the formation of corrosive degradation products and define appropriate residence times for processing using variothermal mold temperature control by oil.

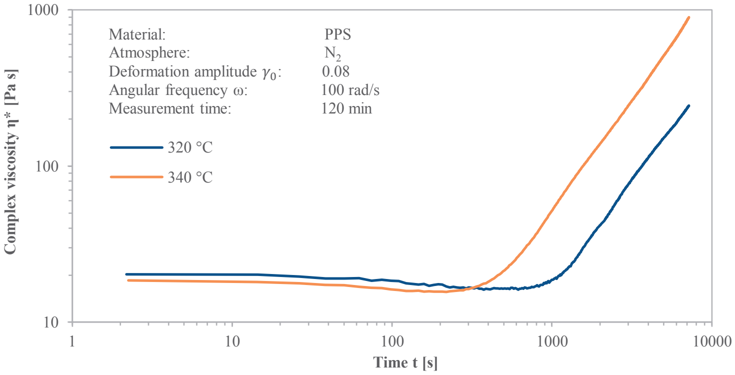


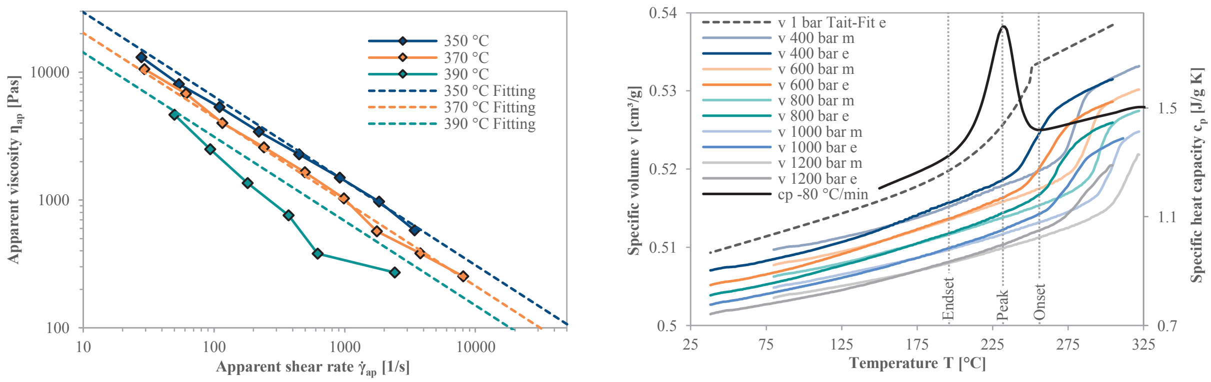
FIGURE 2. Complex viscosity of PPS over time in a double logarithmic scale.

PRE-PROCESSING

Material model

All required material data to calculate filling and cooling, that are shear viscosity, heat capacity during cooling, pvT-behavior and thermal conductivity, of the highly filled compound were measured and converted to an entire material model. Referring to **FIGURE 3 (a)** viscosity data were measured with a capillary rheometer at 350 °C, 370 °C and 390 °C. These temperatures exceed the allowed processing temperatures by far (see **FIGURE 2**), but at lower temperatures the material stagnated within the nozzle preventing any measurements and thus the used temperature levels reflect the possible loads (temperature, shear and shear heating, residence times) acting on the material during injection molding. However, each measurement took 16 minutes. This and the temperature loads imply a degradation of the matrix material. I.e. the high viscosity level in **FIGURE 3 (a)** is a result of the combination of the described degradation respectively aging of the matrix material and filler insertion resulting in polymer-filler and filler-filler interaction [3]. But since the viscosity level of the degraded matrix material is still less than that of other highly filled thermoplastic matrices like PP, the flow of the solid filler in a melt is still feasible. A plateau of zero viscosity at low shear rates is not detectable [2, 4]. Therefore, the viscosity was modelled using the Power law or Ostwald-de Waele relationship [4]. As wall slippage was expressed by pressure variations during the measurements, presumably evoked by decomposition products and influences due to the inlet geometry of the nozzle, and a negative intercept of the function of inlet pressure losses depending on nozzle diameter, correction methods (Bagley [5] or Weissenberg-Rabinowitsch [6]) were not eligible [4]. Thus, only apparent data are available. Additionally, rheology measurements during extrusion with a slot nozzle were carried out. This method was found to be useful only for shear rates smaller than occurring during injection molding, hence not solving the present problems. With this in mind the viscosity model cannot be seen as fix, since on the one hand the level of viscosity and shear rate are obscure because it was not possible to correct the data, on the other hand because the measurement under higher temperatures induces long measuring times and degradation of the matrix material effecting an increase in viscosity level in turn. Due to the fact that the loads may also affect the material during injection molding and thus reflecting reality, the simulation was executed accessing this viscosity model.

The heat capacity was measured by differential scanning calorimetry (DSC). For injection molding simulation the highest cooling rate possible should be provided. **FIGURE 3 (b)** indicates the crystallization peak of the highly filled compound at 230 °C during cooling at -80 °C/min. The isobaric pvT-measurements, which could only be conducted at a lower cooling rate (-2.5 °C/min) with a cylinder-piston dilatometer, indicate a transition area at a higher temperature (280 °C at 400 bar). This inconsistency has to be eliminated. Therefore, the pvT-measurements have been adjusted to the DSC measurement using selected data points as an indicator. Afterwards the extrapolated measurement data were fitted via the 2-domain-modified Tait model [7, 8, 9] also considering pressure dependencies during measuring.



(a) (b)

FIGURE 3. (a) Apparent shear viscosity measured with a capillary rheometer (nozzle with diameter 1 mm and length 20 mm) and fitting according to the Power law equation. (b) Selected measurement points of pvT were extrapolated to a higher cooling rate to correspond to the DSC-measurement of the specific heat capacity. The thus shifted measurements (m = measurement, e = extrapolated/shifted) and the 2-domain-modified Tait model for 1 bar of the highly filled compound are represented.

Geometry model and mesh

As usual a surface mesh of the part was used to create the tetrahedral volume mesh. To identify the best relation in the tradeoff between calculation times and validity of simulation results three meshes with varying element size (Mesh A: 0.3, Mesh B: 0.4-0.5 and Mesh C: 0.5 with simplified geometry without radii etc.) were generated. The occurrence of a frozen skin layer, the highly filled material is prone to form due to the high thermal conductivity, was simulated with boundary layer meshes. The locations of the tempering channels were adopted from the original mold. The characteristic element size regarding the volume meshes of the tempering channels and the mold were kept constant. Since the comparison between the simulation results generated with the different part meshes showed that a discretization of 0.4-0.5 (Mesh B) meets the requirements of this tradeoff in the best way, the following simulations were carried out using this mesh. At each location for measuring cavity pressure during form filling sensor nodes with a distance of 0.1 mm between each other were defined over part thickness. This allows gathering information considering the simulated temperature profile in the part besides the simulated cavity pressure.

Process definition

The properties of the machine data of a fully hydraulic injection molding machine of Arburg Allrounder 470 S 1100-400 35 (multi-component injection molding machine) were already included in the simulation software. In accordance with the maximum injection rate while using the pressure accumulator the value was adjusted to 492 cm^3/s. A realistic injection flow rate profile was used so that the pressure was calculated via flow rate. As the maximal injection rate is reached, the simulation changes to a pressure controlled flow rate modus.

SIMULATION RESULTS

In correspondence to the results gained by the rotational rheometer the melt temperature was set to a fairly low level, but since the high filler loading leads to shear heating inside the nozzle during injection, higher melt temperatures at the sprue gate were also calculated. Preventing the material to form a frozen skin layer at a mold surface a mold temperature of 270 °C has to be provided as additional DSC measurements showed. Nevertheless lower mold temperatures were simulated as well, because the occurring heat loss remains unidentified. The heat transfer coefficients have been varied due to the fact that these data are not available and are dependent on the different injection molding steps, which cause instable contact to the mold. **TABLE (1)** includes all results regarding the target criteria form filling and filling time.

The melt temperature as well as the heat transfer coefficient essentially define whether the form is partially or completely filled. The mold temperature does not seem to have a major influence on the form filling, but as it defines the formation of the skin layer, its effect on the product properties should be kept in mind.

TABLE (1). Critical process parameter (T_{Me} = melt temperature, T_{Mo} = mold temperature, maximal filling pressure: 2500 bar) in dependence on the heat transfer coefficients. The data in the fields correspond to the simulated filling time in s. Here red fields represent a partial form filling and green fields denote an entire form filling.

T_{Me} [°C]	T_{Mo} [°C]	Heat transfer coefficient [W/m²*K]			
		2000	1500	1000	500
340	220	🟥	🟥	🟥	🟥
	240	🟥	🟥	🟥	🟥
	260	🟥	🟥	🟥	🟥
	280	🟥	🟥	🟥	🟥
350	220	🟥	🟥	🟥	🟥
	240	🟥	🟥	🟥	0.9273
	260	🟥	🟥	🟥	0.9105
	280	🟥	🟥	🟥	0.8444
360	220	🟥	🟥	0.9013	0.6485
	240	🟥	🟥	0.7970	0.6270
	260	🟥	🟥	0.7384	0.6088
	280	🟥	0.8269	0.6871	0.5944
370	220	🟥	0.7701	0.5183	0.4338
	240	🟥	0.6049	0.4928	0.4277
	260	0.7393	0.5476	0.4733	0.4204
	280	0.5831	0.5079	0.4540	0.4126
380	220	0.5452	0.3854	0.3329	0.2985
	240	0.4388	0.3638	0.3243	0.2966
	260	0.3880	0.3465	0.3162	0.2910
	280	0.3603	0.3314	0.3075	0.2888

CONCLUSION AND FUTURE WORK

Using injection molding simulation on a test specimen adapting the flow conditions during injection molding of a bipolar half plate were investigated to define the required process conditions to fill the cavity. Therefore, a material model of a highly filled PPS compound was compiled. Since the measurements of viscosity as well as heat losses and heat transfer coefficients are ambiguous, a reference process with preferably low melt temperatures, high mold temperatures and low heat transfer coefficients has to be temporized to build up a broad (process calibrated [10]) simulation model including variothermal mold heating. Under these aspects long computing times simulating the whole injection molding process (various cycles with preparation, filling and cooling) are justified.

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