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FACULTY OF MECHANICAL ENGINEERING
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A COMPREHENSIVE DEVELOPMENT OF A PVT MEASUREMENT METHOD

THESES BOOKLET OF PHD DISSERTATION

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The evaluation of the dissertation and the protocol of the defense can be viewed at the Dean's Office at the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics

1. Introduction and goals

In the 20th century, the importance of artificial polymers increased considerably in developed societies, and this tendency seems to continue at the beginning of the 21st century. Today more than 30% of thermoplastic materials are processed by injection molding. Injection molding is one of the most dynamically developing batch process used in manufacturing polymer finished products. Three-dimensional complex geometry, even large parts can be produced economically and practically without waste with injection molding, therefore the technology is used more and more often to manufacture among others technological and household parts, automotive parts, toys, packaging materials and medical devices.

The final properties of injection-molded parts are determined by many factors, therefore because of the complexity of the process, much research has been done to understand the processes during manufacturing, and modeling them as accurately as possible. Nowadays injection molding simulation programs are more and more widely used because they enable virtual injection molding without actually manufacturing a mold. The development of computer technology, simulation algorithms and strong competition have greatly contributed to this. The economy of injection molding, the final price of the product and the time the product gets to the market are greatly influenced by how efficiently numerical simulation processes can aid the designing of the part and the injection mold. Injection molding simulation programs such as Moldflow, attempt to decrease the danger of manufacturing parts with inaccurate dimensions or shape, and decrease the number of mold modifications necessary for the manufacturing of the product according to customer demands by providing a quantitative prediction based on the data available. Based on the obtained results the product, the mold, the material and most of the processing parameters can be optimized, but accurate material data is necessary for usable results. In many cases simulation programs are used with estimated data or average values, which can be attributed to the costly measurement of material properties.

In the numerical simulation of the injection molding process, the pressure-volume-temperature relationship (pvT data) of the material is among the most important input data but also one of the most difficult to measure. This is why it is important that the pvT data available describe the behavior of the material as accurately as possible because this is necessary for calculations, predictions and estimates of proper accuracy and correct optimizations.

Procedures widely used for measuring pvT data are slow, measurements can last days, and the measurement of polymers prone to thermal degradation require special attention. Often the accuracy of measurements is not sufficient, either. Some of the inaccuracies can be attributed to the errors of the measurement principles; others are caused by the fact that measurement parameters are very different from injection molding parameters.

The main goal of my PhD dissertation is to work out and analyze a measurement principle which allows the measurement of specific volume (not characteristic of the equilibrium state) of thermoplastics, in injection molding conditions, with the help of an injection molding machine. A great advantage of the new measurement principle is not only that the measurement process is a great deal faster but also that the results are much closer to real life because measurement takes place in processing conditions, on the injection molding machine itself.

2. A critical analysis of the literature, clarifying the goals

Injection molding is one of the most important and versatile technologies to produce polymer parts. Because of the behavior of the materials and the technology, the material undergoes a considerable change in specific volume, which must be known for the technology and the designing of parts.

The behavior of polymers is basically determined by their chemical structure, as a result of which there is a considerable difference between the pvT properties of amorphous and semi-crystalline polymers. What is common in them, however, is that the specific volume of both kinds of materials depends heavily on temperature (a thermal expansion coefficient an order of magnitude higher on average than that of metals), pressure (considerable compressibility even in solid state), and cooling rate. Based on my research of the literature it can be stated that the widely used methods to determine pvT properties, such as direct and indirect dilatometry, cannot provide pvT data characteristic of the thermal conditions of injection molding or extrusion, since the cooling rate achievable during measurement can be several orders of magnitude higher than during processing technologies.

In the past, several studies have focused on special measuring equipment that is suitable for the examination of the effect of cooling rate, but the cooling rate achieved is often lower than the cooling rate characteristic of injection molding. Another problem is that cooling rate was not properly controlled in every case. Since polymers are poor conductors of

heat, another problem in the case of high heating and cooling rates is the great temperature difference in the sample, which in the case of larger samples can even exceed 100°C. In spite of this, some authors ignore the temperature inhomogeneity in the sample in the case of higher cooling rates, which negatively affect the accuracy of measurements.

Several authors developed measuring systems based on extrusion, but these only work above the transition temperature range, and also, the maximum of the measurable pressure range is an order of magnitude narrower than the range characteristic of injection molding. In order to increase the pressure range of measuring, several authors focused on measuring the pvT properties in the injection unit of the injection molding machine. This measurement method was, however, considered unsuitable because the results differed considerably from the results of the conventional measuring method due to higher pressures.

Another problem is that several measuring methods can be found in the literature for the analysis of pvT properties with possible differences in the measurement results and measurement errors can also occur, especially when the transition range is determined. Only pvT curves obtained with isobar cooling can be used for injection molding simulations and to examine the injection molding process, since only in this can it be ensured that the examined transition will be solidification during injection molding and pressure changes cannot influence the transition process.

Today finite element algorithms gain more and more importance since they can speed up the design process and many of the errors can be eliminated before manufacturing. pvT data are indispensable for all widely used shrinkage models and therefore for finite element algorithms, too. The input data of algorithms affect the end results so it is very important that pvT data describe the behavior of the material during processing as accurately as possible. Since the equations of state used to describe pvT data most often can only characterize the behavior of the material according to the conditions of measurement, it is very important that measurement be carried out in conditions similar to processing.

Based on the literature study I set the following goals for my dissertation:

- to develop a new measurement process using which the pressure-volume-temperature (pvT) relationship of thermoplastic polymers can be measured in injection molding conditions (not equilibrium conditions),
- to design, build and test measuring equipment to investigate the practicability of the newly developed measuring principle,
- to develop and test the algorithms necessary to evaluate the measurements,

- to optimize the operation of the equipment and compare the measured pvT data with measurement results of other measurement methods,
- to examine the cooling rate in the case of amorphous thermoplastic materials, to use the pvT data obtained with high cooling rates in simulation algorithms and to analyze their effect on the accuracy of calculation.

3. Methods of investigation and results

I developed a new measurement principle, which measures specific volume by measuring shrinkage after the polymer melt is injected into the mold. To prove the viability of the new measuring method, I designed and made a special injection compression mold insert (Fig. 1.).

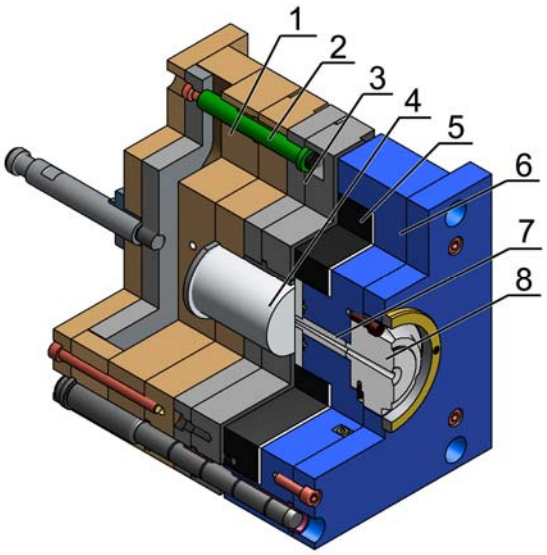

Fig. 1. The structure of the special injection compression mold used for the measurements (1-movable platen, 2- pulling rod, 3- sliding plate, 4- core, 5- electromagnet, 6- stationary platen, 7- replaceable sprue element, 8-pneumatic nozzle inzert)

The mold cavity of the measuring tool I developed can be changed in a stepless manner over the whole measuring cycle, which is made possible by a movable core in the tool. The different measuring pressures can be achieved by exerting forces of various magnitude on the movable core. The volume change of the material in the mold cavity can be calculated from the displacement of the core.

After analyzing the first results, I divided the measuring process into two parts to increase the accuracy of the measured data. In the first phase of measurements, I examined the range above the glass transition temperature with the injection unit of the injection molding

machine, then I examined the characteristic behavior under the transition range with the special injection compression mold.

When measurements were carried out in the injection unit, I experienced considerable differences between data measured in the conventional way and data measured in the injection molding machine in the range of higher pressures (40-120 MPa), which was in accordance with the literature. In order to improve the accuracy of measurements, I examined the phenomena during measurement that can lead to significant measurement errors if ignored. Based on my investigation I recommended corrections based on physical bases to eliminate the factors that I believe cause the most significant measurement errors. I examined the effect of the parameters of plasticizing on the specific volumes measured in the injection unit in the case of ABS materials. I found that an incorrect setting of the parameters of the plasticizing process (peripheral speed of the screw, back pressure, residual time) can cause significant measurement errors. I proved that with the proper plasticizing settings, with the corrections I recommended, it is possible to determine accurate pvT data in the injection unit even in the range of higher pressures, as opposed to what is found in the literature (Fig. 2.).

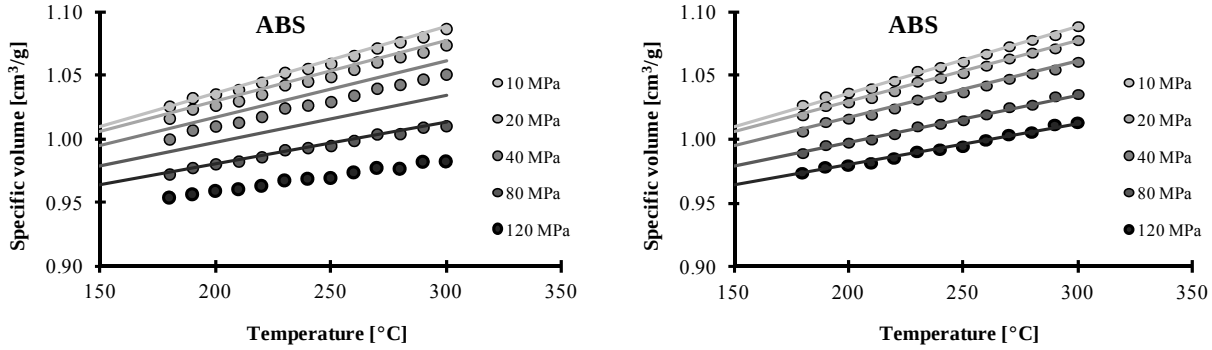

Fig. 2. Points measured in the injection unit of the injection molding machine on ABS, specific volume values without correction (a) corrected specific volume values (b) compared to data determined with the Confining Fluid method (lines)

Due to the high cooling rate, there can be a considerable (even exceeding 100°C) temperature difference between the outer and inner parts of the sample, therefore the data measured in the injection compression mold cannot be connected to a temperature and pressure directly. I developed a correction method to determine the specific volume belonging to the individual temperatures. The calculation can be done with the volume-time relationship measured in the special mold and the temperature distribution. I used the explicit approximation method to solve the differential equation of thermal conduction. I proved with

measurements in the injection compression mold with thermodynamic calculations that different cooling rates can be achieved with different sample thicknesses. With samples of 5-1 mm thickness, I was able to vary cooling rate at the glass transition temperature in the range of 115-6500°C/min in the case of the materials I used.

I proved that in the pvT measurements based on injection compression molding there is a material-dependent compression limit pressure (Fig. 3) above which the glass transition temperature and its pressure dependence can be determined more accurately. I used a method based on extrapolation to obtain the glass transition temperatures at lower pressures more accurately, which helped decrease the uncertainty of results at 10 and 20 MPa considerably.

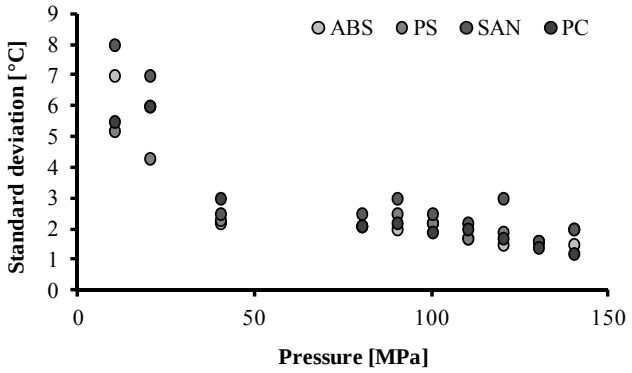

Fig. 3. The uncertainty of measurement of the glass transition temperatures determined for various pressures

The specific volumes of thick samples (low cooling rate) show a good correlation with the data obtained with the conventional method (Fig. 4.).

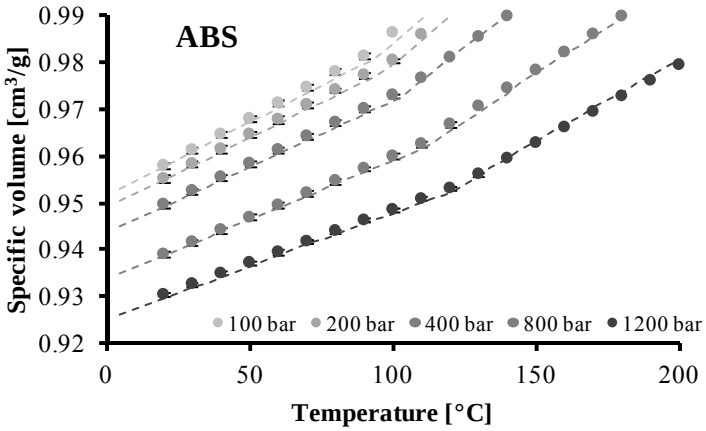

Fig. 4. Specific volumes measured on ABS samples of 5 mm thickness (dots) compared to data measured with the conventional method (dashes)

I proved with tests on amorphous thermoplastics at different cooling rates that the new measurement process is capable of showing the shift in the glass transition temperature and the increase in specific volume as the cooling rate is increased (Fig. 5.).

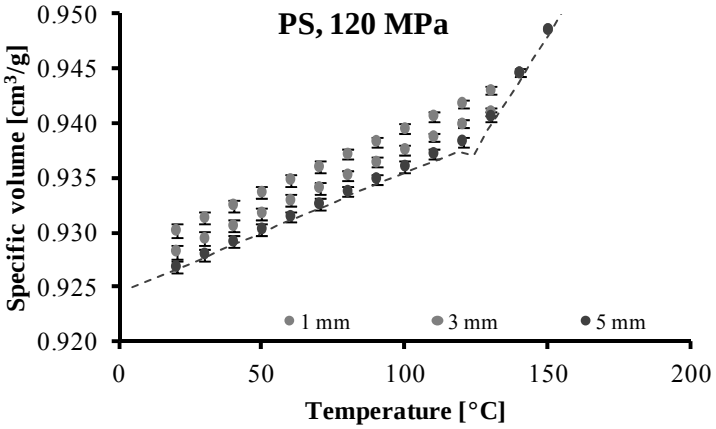

Fig 5. Specific volumes measured on 5, 3 and 1 mm thick polystyrene (PS) samples, at different cooling rates, at a pressure of 120 MPa (dots), compared to data obtained with the conventional method (dashes)

I examined the effect of pvT data obtained at different cooling rates on simulations by carrying out shrinkage calculations for several different technological settings using several pvT data series obtained at different cooling rates. Then I compared the calculated data with the measured shrinkage of actual parts injection molded with the technological settings used in the simulations. I proved that the algorithm, using the data obtained with high cooling rates, can predict the shrinkage of a thin-walled (1.2 mm), plate-like part more accurately compared to the actual measured data than the Confining Fluid method (Fig. 6.).

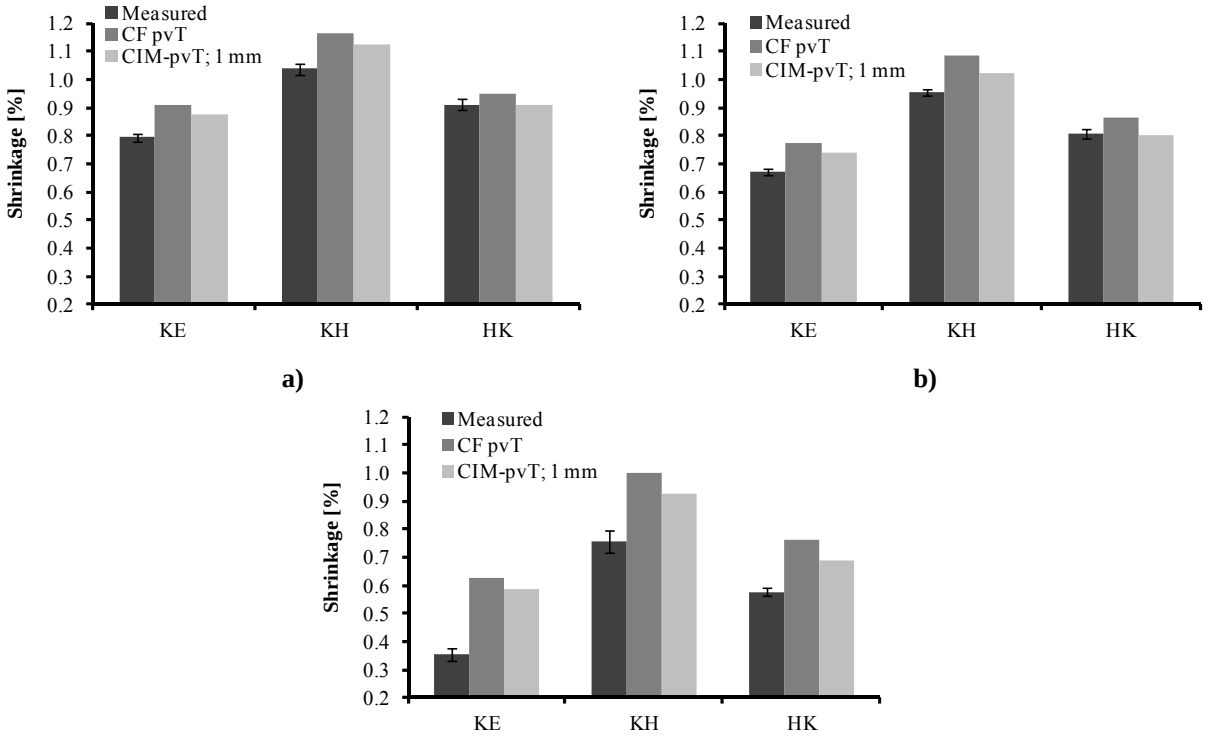

Fig. 6. The real and calculated shrinkage of 80x80x1.2 mm BASF Terluran GP-35 injection molded samples at a melt temperature of 240°C and a mold temperature of 40°C, and at holding pressures of 300 bar (a), 500 bar (b) and 700 bar. The calculation was done with used simulation and pvT data measured with different methods (CF pvT: Simulation with pvT data measured with the Confining Fluid technique; CIM-pvT; 1 mm: Simulation with pvT data from my own measurement on a 1 mm thick sample; KE – shrinkage across the sample at the front, KH - shrinkage across the sample at the back, HK – longitudinal shrinkage in the middle)

4. Theses

I summarize my research in the following theses:

Thesis 1:

I developed a special measurement method based on injection compression molding. The measurement can be performed on an injection molding machine. I also developed an evaluation algorithm for it, with which the pressure-volume-temperature relationship of amorphous thermoplastics can be calculated between 20-350°C and 10-180 MPa in two steps and in actual processing conditions. The data for the range above the glass transition temperature range were calculated with a mathematical model I created from data measured in the plasticizing unit of the injection molding machine, while data for the range under the glass transition temperature range were calculated with the mathematical model from data measured in a special injection compression mold. I proved the applicability of the measurement principle for polystyrene, styrene copolymers (ABS, SAN), and polycarbonate by comparing the calculations with indirect dilatometer measurements [1-3, 5, 6].

Thesis 2:

I proved that with the compensation of the deformations in the injection unit due to mechanical and thermal effects, the effect of the dead spot before the screw tip and the mechanical work done on the sample during measurement, and the minimization of the temperature rise of the melt created by plastication, the specific volume of thermoplastic melts can be determined at an accuracy of 0.3% in the range of 10-120 MPa with measurements in the injection unit. I proved this with an Arburg Allrounder 370S 700-290 Advance injection molding machine for polystyrene (PS) and styrene copolymers (ABS, SAN) in the temperature range 180-300°C, and for polycarbonate (PC) in the temperature range 250-340°C [2, 3, 6].

Thesis 3:

I showed that the measuring system based on injection compression molding that I developed is capable of determining the pressure-volume-temperature relationship under the glass transition temperature range using isobar cooling. I proved that in the case of amorphous

thermoplastics the calculation can be done in the compression phase from the temporal change of the wall thickness of the sample and its cross-sectional temperature distribution. I proved my thesis using polystyrene, styrene copolymers (ABS, SAN), and polycarbonate [1-3, 5, 6].

Thesis 4:

I proved that in injection compression molding pressure-volume-temperature measurements there is a compression limit pressure, which depends on the material. Above this limit, the glass transition temperature and its pressure dependence can be determined more accurately. I proved that from these measurements the parameters describing the glass transition temperature and its pressure dependence of the double-range Tait equation can be calculated and can be used to improve the accuracy of data calculated under the limit compression pressure. I proved this using polystyrene, styrene copolymers (ABS, SAN), and polycarbonate.

Thesis 5:

I proved that in the case of amorphous thermoplastics specific volumes for different cooling rates can be obtained with the measurement of samples of different wall thicknesses at isobaric cooling. The accuracy of the prediction of shrinkage can be improved with calculations using specific volume data obtained from measurements in the cooling rate range characteristic of injection molding.

5. References

1. **Szabó F**., Kovács J. G.: Development of a novel pvT measuring technique. Material Science Forum, 729, 126-131 (2013).
2. **Szabó F**., Kovacs J. G.: Development of a pressure-volume-temperature measurement method for thermoplastic materials based on compression injection molding. Journal of Applied Polymer Science, 131, 41140-41148 (2014).
3. **Szabó F**., Kovács J. G.: Új lehetőségek a pvT tulajdonságok meghatározására: a CIM-pvT rendszer. Műanyag és Gumi, 51, 47-51 (2014).
4. Suplicz A., **Szabo F**., Kovacs J. G.: Injection molding of ceramic filled polypropylene: The effect of thermal conductivity and cooling rate on crystallinity. Thermochimica Acta, 574, 145-150 (2013).
5. Suplicz A, **Szabó F**., Kovács J G: Anyagvizsgálati módszerek fejlesztése fröccsöntési alkalmazáshoz. Műanyagipari Évkönyv, 11, 34-41 (2013).
6. **Szabó F**., Suplicz A., Kovács J. G.: Anyagtulajdonságok újszerű mérési lehetőségei. Nemzetközi Gépészeti Találkozó - (OGÉT), Arad, Románia, 350-353 (2013).
7. **Szabó F**., Tábi T.: Optimization of the injection moulded PLA-cellulose composite products. Proceedings of the Seventh Conference on Mechanical Engineering, Budapest, Hungary, p6 (2010).
8. Tábi T., Sajó I. E., **Szabó F**., Luyt A. S., Kovács J. G.: Crystalline structure of annealed polylactic acid and its relation to processing. Express Polymer Letters, 4, 659-668 (2010).
9. Suplicz A., **Szabó F**., Kovács J. G.: Hővezető polimerek fejlesztési lehetőségei és vizsgálati módszerei. Nemzetközi Gépészeti Találkozó - (OGÉT), Arad, Románia, 346-349 (2013).
10. Zink B., **Szabó F**., Hatos I., Hargitai H., Kovács J. G.: DMLS szerszámbetétek szimulációs vizsgálata. Műanyag- és Gumiipari Évkönyv, 12, 80-87 (2014).
11. Tábi T., Suplicz A., **Szabó F**., Kovács N. K., Zink B., Hargitai H., Kovács J. G.: The analysis of injection molding defects caused by gate vestiges, Express Polymer Letters, 9, 394-400 (2015).