Development of a Novel Pvt Measuring Technique
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Development of a novel pvT measuring technique

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Abstract. The pressure-temperature-specific volume relation of polymers is important not only for physical chemistry, but they are very significant input data for injection molding simulation software. Today's methods for measuring pvT data are slow, measurements can take days to be carried out, and in many cases the accuracy of the measurement is unsatisfactory. In our work, a new measuring method has been developed which makes the determination of the pvT relation faster compared to conventional processes within injection molding processing conditions. For the measurements a special injection mould was developed, in which the pvT relation of the material can be determined from the shrinkage in the mold. The data measured by the new method using polypropylene at a mold temperature of 23°C were compared to the data given in the database of the simulation software.

Introduction

In order to obtain the increasing requirements against injection-molded products, simulation methods gained more significance the past few years. Considerable amount of time and money can be saved by the use of simulation software, if proper information can be provided of the expectable shrinkage, warpage and other possible defects of the final product. The most commonly used input parameter on which the simulation process is based is the pressure-volume-temperature relationship of the resin [1].

The most common technique applied for the measurement of the pvT properties are the piston-die and the confining fluid technique. In piston-die technique the sample is enclosed into a rigid cylindrical chamber, which is bounded by a fixed piston from the bottom, and a movable piston from the top. The leaking of the material between the pistons is prevented by PTFE sealing. The heating of the material is carried out by electric heating, while the cooling is provided by pressurized air. The setting of the appropriate pressure is reached by the displacement of the movable piston, and therefore the change of volume can be measured. The advantage of this method is the simplicity of the measuring device. The disadvantage is that according to the friction of the wall of the cylinder, the pressure is not hydrostatic [2].

During the confining fluid technique the sample is also placed into a rigid chamber, which is closed by bellows. The sample is submerged into mercury or silicon oil therefore the obtained pressure will be hydrostatic. The heating of the cylinder is electric, the appropriate pressure can be reached by putting the liquid under pressure, and thus the change of the specific volume can be determined by measuring the deformation of the bellows. The advantage of the method is that the utilized pressure is hydrostatic. The disadvantage is that the liquid and the sample could get into reaction and that the measured data has to be compensated in order to take into consideration the change of the specific volume of the liquid [2, 3].

According to Luyé [2] the different circumstances could cause unlike results of the measurements of the piston-die and the confining fluid techniques. The difference is more significant at glassy polymers of small Poisson coefficient, great tensile strength. The common property of the two conventional methods is that the measurement needs quite long time and the achievable

heating/cooling rate is low, usually a few 10°C/min. This is much less than cooling rates during processing technologies. In 1977 Menges [4] has already presented that the specific volume of amorphous and semi-crystalline polymers as well depends on not just temperature and pressure, but is also dependent of the cooling rate. In case of semi-crystalline materials the melting and the crystallisation temperature always differ from each other because of thermodynamic reasons, as a result the difference between the results of the measurements can be significant depending on the material being heated or cooled during the analysis. The crystallization temperature is highly dependent on the pressure, the given additives, the cooling rate and the orientation of the chain [4-6].

Luyé [2] showed the deficiencies of the commonly used pvT measurement methods and proved that the pvT data measured during isobar cooling is the only one that could be used for injection-molding simulation. He gave a detailed explanation that with high cooling rate the temperature gradient in the sample has a great affect on the results of the measurement.

During the last few years several methods were presented which enable the pvT properties to be measured with higher cooling rate or even during the processing of the material:

Chakravorty [1] modified a piston-die based instrument, that the pvT properties could be examined under higher cooling rates (even 200°C/min). Van der Beek et al. [6] combined a piston-die device with a Couette viscosimeter. The modification enabled the examination of the effect of not just the pressure, the temperature and the cooling rate on specific volume, but the effect of shearing. Forstner [7] further developed the invention of van der Beek and achieved a cooling rate of 100°C/sec.

Nunn [8] used the injection barrel of an injection-molding machine to measure pvT. He plugged the barrel and by the screw he compressed the resin. Rogelj and Krajnc [9] built a special nozzle which can be put onto the injection-molding machine. With this nozzle the behavior and the pvT properties of the polymer melt during fast compression and expansion could be examined. Wang et al. [3] built a special injection mould which enabled the examination of amorphous and semi-crystalline materials applying isobar heating.

Sadeghian et al. [10] used an extruder to determine the pressure-temperature-specific volume relations in case of HDPE-wood-fiber composites. Park et al. [11] utilized an extruder and a gear-pump to get information about the pvT data of polymers and polymer-foams.

Li et al. [12] developed a pvT measuring method for PP/CO_2 systems based on optical image recognition. Kim et al. [13] examined the usability of ultrasonic velocity measurement in the determination of pvT properties, and also the possibility to use ultrasonic techniques to predetermine the mass and the modulus of molded products.

To sum up, conventional measurement methods cannot provide appropriate pvT data within the thermal conditions of injection-molding. The special processes are either not able to cover the temperature range of processing or apply fast cooling, but does not take into consideration the temperature gradient of the sample, or cannot do examinations for the changes appearing during injection-molding. As a result the aim of this article is to develop a method by which the measurement of the pvT data could be carried out within the thermal conditions of injection-molding.

New method for measure pvT

During injection-molding the injected polymer melt is being cooled down in the mould, while its specific volume changes. During the making of a product this specific volume change could be partially compensated by putting the melt under pressure during the packing phase. The basis of this new measuring process is that the specific volume is measured using the shrinkage of the part in the mould. This measurement can be carried out in a special injection mould, in which the shrinkage of the part caused by the change of specific volume can be compensated and measured with a movable core. Knowing the cross sectional area and position of the core the change of volume can be calculated, and by measuring the mass of the material the specific volume can also be determined.

The first step of the measuring process is injecting the melt into the mould cavity. Similar to other pvT measurement techniques the leaking of the material during the measurement has to be prevented by closing the gate and using proper fitting. The next step is building up the required pressure and measuring the temperature and the displacement of the core during the cooling. After that the specimen is removed and its mass is measured. Some corrections have to be made as well during the processing of the obtained data, because the temperature distribution in the specimen caused by the fast cooling cannot be neglected. Since thermal conductivity of polymers is very poor, the temperature difference between the centre and outer parts of the specimen can reach 100°C. For this correction the temperature distribution of the specimen has to be known throughout the whole measurement process, which can be obtained by simulation or analytical calculation. Further compensation is necessary because of the volumetric change of the mould cavity, and the expansion as well. Since these factors are causing much smaller error than the temperature distribution, they were neglected during the measurements carried out.

To demonstrate the usability of the measuring method, an experimental mould was designed (Fig. 1.). Throughout the designing the main concept was to assure the simplest construction that is possible, and to be able to set the thickness of the specimen. For the ease of forming and having good thermal conductivity the mould was made of aluminum. In the first stage of the measurement the melt flows through the stationary plate (Fig. 1./1) towards the valve (Fig. 1./4). The pressure of the melt opens the valve and flows forward, towards the cavity (Fig. 1./3). The cavity ends in a movable core (Fig. 1./2). After filling the cavity, the pressure decreases in front of the valve and the spring (Fig. 1./5) closes the valve. In the cavity the pressure can be controlled by the movable core, displacing by the ejection system. The thickness of the sample can be modified with screw (Fig. 1./6). The diameter of the samples was 30 mm and their nominal thickness was 4.5 mm.
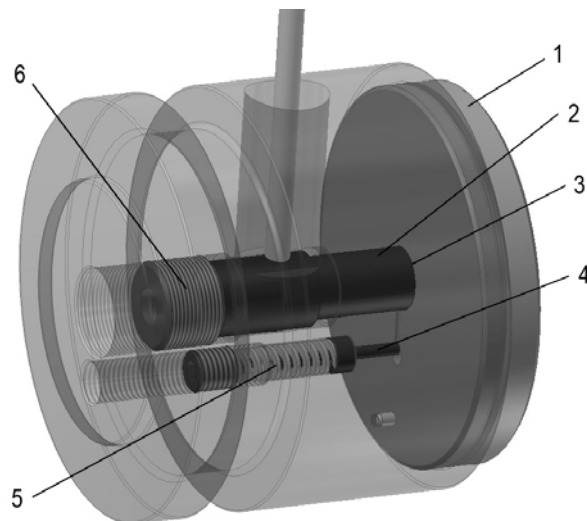

Fig. 1. The 3D model of the experimental mold
(1-stationary plate; 2-movable core; 3-the cavity; 4-valve; 5-spring; 6-adjusting screw)

In the measurement the friction was neglected and the pressure was calculated as the ratio of the ejection force and the cross sectional area of the mould cavity. The change of the specific volume can be calculated by the core position. A Ni-Cr thermocouple was installed in 1 mm depth from the cavity surface, to measure the change of the temperature. The accuracy of the sensor, which measured the displacement of the core, was 0.001 mm. The experimental trials were carried out on an injection molding machine made by Arburg GmbH Co. (Allrounder 470H 1000-250). The applied polymer was Borealis RJ470MO polypropylene. The pvT data of this polypropylene is given in Moldflow software.

Results and discussion

During the measurement the thickness of the specimens (which have the same mass) was measured on different pressures as a function of the time. Since the cross sectional area of the specimen is constant during the measurement, the change of thickness is linear to the change in specific volume. The starting moment (zero) was considered to be the moment when the required pressure was built up. Fig. 2. shows the displacement of the core in the case of weighted samples made at 70 and 420 bars pressure.
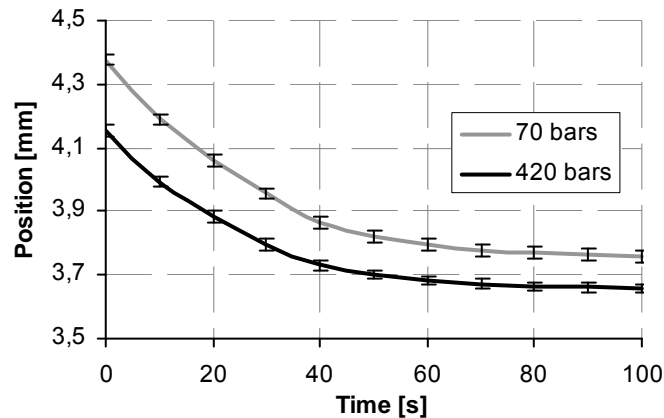
Fig. 2. The position of the core

It can be seen that the curves belonging to different pressure are clearly different and the differences can be well measured. At 70 bars the thickness of specimen changed from 4.38 mm to 3.75 mm during the cooling which means a more than 14% change. This is smaller than the data calculated based on the Moldflow database. By raising the pressure in the cavity with 350 bars, the specific volume of the polymer changed by 2.7% after solidification, which is greater than given by the manufacturer. The differences are probably caused by the totally different conditions of the measurement, which causes significant differences in the degree of crystallinity of the specimen as well. The measured curves at different pressure show that in accordance with the cooling of the specimen the distance between the curve decreases, which can be explained by the change in compressibility.

To build up a model for the temperature distribution of the specimen it is necessary to know the temperature of the mould cavity during the measurement cycle. The temperature of the mould cavity was measured throughout more cycles at a distance of 1 mm from the wall which is in connection with the specimen (Fig. 3.).
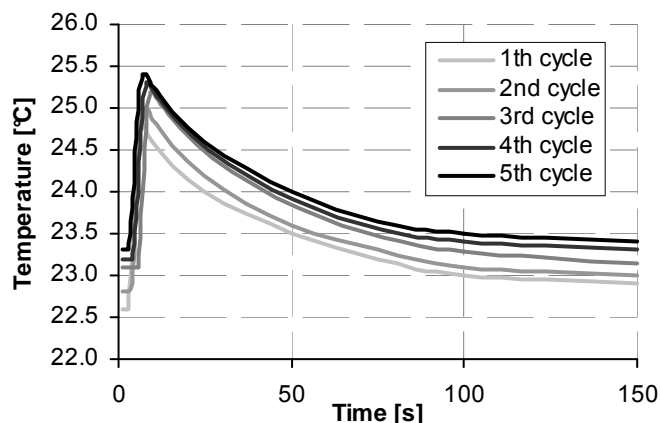
Fig. 3. The temperature variation of the mold

It can be seen that after the injection the wall temperature of the mould raises by 1.5-2°C, than rapidly decreases to the original value. Due to the moderate temperature rise the mould wall temperature can considered to be constant during the simulation of the cooling. With taking into consideration the temperature distribution of the specimen, the evaluation of the results is very complicated. The current model contains simplifications, so the temperature distribution is neglected. Since cooling the temperature of the specimen is uniform and equal to the mould temperature, so its specific volume at different pressure can be determined (Fig. 4.).
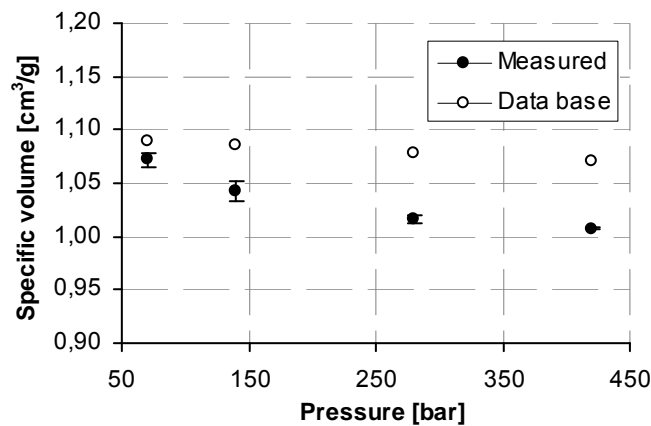

Fig. 4. The specific volume of Borealis RJ470MO at 23°C

The deviation of the measured specific volumes in the investigation range of 70-420 bars is insignificant. Comparing these results Moldflow simulation software data, it can be found that this new method resulted in lower specific volume at any cases. The measured values show monotonous decreasing trend by increasing the pressure. However the rate of decreasing, which is in relationship with compressibility, is higher than the results of the software data. The difference between the measured and calculated values varies between 1.7 and 6%

Conclusions

In this work the prevailing pvT measurement methods and their deficiencies was introduced. We developed a new measurement method which is convenient for measuring the pvT properties within the thermal conditions of injection-molding with the help of an injection-molding machine. By this new measurement process the pvT data can be calculated from the shrinkage. We carried out some experiments by a special injection mould, using Borealis RJ470MO polypropylene at a range of 70-420 bars. The measured specific volumes show a monotonous decrease with increasing pressure, and the deviation is small. The measured data was compared the calculated values from the Moldflow database, and resulted that the measured results were 2-6% lower than the calculated. The differences are probably caused by the different conditions of the measurement, which can result in significant difference in the degree of crystallinity of the specimen as well.

Acknowledgment

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