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**Development of a pressure-volume-temperature measurement method for thermoplastic materials based on compression injection molding**

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**Abstract**

The pressure-volume-temperature (pvT) relationship of polymers is vitally important information in designing and manufacturing polymers. Due to the special behavior of polymers, however, it is extremely difficult to accurately measure the data in a way that matches the thermal conditions of injection molding, one of the most widely used processing methods. As neither widely used, commercially available measuring devices, nor special equipment mentioned in the literature can fully satisfy this need, it was decided to build a new device able to determine the pvT relationship during injection molding of the polymer. The new device consists of a special mold that can be used on an injection molding machine and a data collection system connected to it. With the help of this device, pvT data can be measured during processing according to the thermal conditions of injection molding, and also considerably faster, and even in an industrial setting.

**Keywords**

Applications, Theory and Modeling, Thermal Properties, Molding, Manufacturing

**Introduction**

The pressure-volume-temperature relationship of polymers is not only a very important material property of polymer physics but also one of the most important input parameters of injection molding simulation programs [1, 2]. Exact pvT data are necessary when studying mixing properties, or phase changes, and also when the appropriate processing parameters are selected, as well as in simulation procedures to predict the expected shrinkage of the product [2].

Nowadays there is considerably less time available for the development of products than before, which has resulted in a growing emphasis on finite element simulations in the industry. Simulation algorithms require accurate data of the polymer material in order to achieve the desired accuracy, which cannot always be ensured due to the costly and time-consuming measurements of material properties. This is also true for the pressure-volume-temperature relationship, whose measurement is one of the most complicated and costly of all material property measurements. At present, two techniques are widely used to determine the pressure-volume-temperature relationship: the confining fluid and the piston-die procedure [3, 4].

In the piston-die method the sample is placed in a rigid cylindrical chamber with a stationary piston at the bottom and a movable piston at the top. The sample holder is heated electrically, and typically cooled with air. Pressure is exerted on the sample with the movable piston. Leaking of the sample between the pistons is prevented with PTFE insulation. After the mass of the sample is measured, the change in specific volume can be calculated from the movement of the piston. The advantage of the method is that it requires simpler measuring equipment and measures the change in the specific volume of the sample directly. The disadvantage is that the pressure in the measuring chamber is not hydrostatic owing to the friction on the walls of the measuring chamber [3, 4].

The confining fluid technique also uses a rigid chamber to hold the sample. The chamber is covered with a flexible membrane. The sample is surrounded with mercury or silicone oil, therefore the applied pressure is purely hydrostatic. The whole system can be heated electrically and pressure on the sample can be created by exerting pressure on the surrounding liquid. The change in the specific volume of the sample and the surrounding liquid can be calculated from the change in shape of the flexible membrane. As the mass of the sample and the pvT properties of the surrounding liquid are known, the specific volume of the sample can be calculated. The advantage of the method is that the applied pressure is purely hydrostatic, while the disadvantage is that there can be a chemical reaction between the sample and the

liquid, and also, the change in the specific volume of the sample is not measured directly, which involves extra calculations [3, 4].

In both procedures the maximum achievable cooling rate is a few times  $10^{\circ}\text{C}/\text{min}$ , which is several orders of magnitude lower than the cooling rates encountered during injection molding [1]. Since the equations of state describing the change in the specific volume of polymers cannot handle the effect of cooling rate, it is important that measurements are made in real-life processing conditions. A change in the cooling rate can result in significant structural changes in both amorphous and semicrystalline polymers, which can significantly influence pvT properties as well. Above the transition temperature range the effect of cooling rate is negligible but at the transition temperature and below the specific volume depends not only on pressure but to a great extent on the cooling rate as well. In the case of semicrystalline polymers the cooling rate has far greater influence as the change in the cooling rate does not only change the free volume of the amorphous parts, but also the proportion of crystalline parts [4-7].

Recently several authors have pointed out the shortcomings of the widely used pvT measurement methods, the errors that can occur during measurement and the effect pvT data measured in different ways have on simulation results [1, 3, 8].

According to Luyé [3], if measurement is performed with a high cooling rate, the temperature gradient in the sample influences measurement results considerably, therefore neglecting the temperature gradient causes a significant error. He also pointed out that only pvT data measured with isobaric cooling can be used for injection molding simulations, since curves produced with other methods do not produce accurate results due to the characteristics of injection molding and the measurement errors that occur. Gordillo [8] proved that in the injection molding simulations of semicrystalline materials, the programs produce more accurate results with pvT data measured at a higher cooling rate ( $5.4^{\circ}\text{C}/\text{s}$ ), than with data measured at a lower cooling rate ( $0.02^{\circ}\text{C}/\text{s}$ ). Chang et al. [9] analyzed the effect of pvT data on simulations with an injection molded PS lens, Wang et al. [10] analyzed the usability of pvT data measured with a mold and isobaric heating, but their measurement data had extremely high standard deviation.

Recently several scientists have tried to perform pvT measurements during processing, measure the data at higher cooling rates, or investigate effects not analyzed before. Nunn [11] points out that additives can considerably influence the pvT properties of the resins, and so considers it important to develop a measurement method that can be used in industrial settings, too. The injection unit of an injection molding machine was used for the

measurements. After blocking the nozzle, the melt was compressed using the screw. Rogelj and Krajnc [12] built a special nozzle that could be attached to an injection molding machine, which enabled them to examine the pvT properties of polymer melts in close to adiabatic conditions. Wang et al. [13] built a special injection mold for their measurements and used the clamping force of the machine to create a pressure necessary for measuring. Their measurements were carried out with isobaric heating, which is completely different from the conditions during injection molding, as Luyé pointed out.

Sadeghian et al. [14] used an extrusion system to determine the pressure-volume-temperature relationships of HDPE composites reinforced with wood fibers. Park et al. [15] used an extruder and gear pump to determine the pvT properties of polymers and polymer foams. In both methods, due to the extrusion measuring method the temperature and pressure ranges are much narrower than in the case of injection molding, therefore the data obtained is not accurate enough for injection molding simulation.

Chakravorty [1] converted a device using the piston-die principle so that the device could handle far higher cooling rates (up to 200°C/min), however, after measuring the pvT properties he did not apply compensation to eliminate the effects caused by temperature differences in the sample. Van der Beek et al. [16] combined a piston-die device with a Couette viscosimeter. The conversion made it possible to examine the influence of shear in addition to pressure, temperature and cooling rate on specific volume. The thickness of the sample was decreased to reduce the impact of temperature distribution. Forstner [17] further developed van der Beek's equipment and achieved a cooling rate of 100°C/s. Li et al. [18] developed a pvT measuring device based on optical image recognition for PP/CO<sub>2</sub> systems but their system is not able to examine the effects of cooling rate. Kim et al. [19] examined the connection between the propagation speed of ultrasound and pvT properties and showed good correlation, but they did not examine the effects of cooling rate. Kowalska [20] used pvT data measured with the conventional piston-die technique and crystallization kinetics modeling to calculate pvT data in high cooling rate conditions. Since neither widely used methods (Confining fluid and Piston-die), nor specially developed procedures are able to provide pvT data that fit the conditions during injection molding in every respect, we have set the goal of creating a new procedure which makes it possible to measure pvT data in a way that is very similar or identical to the conditions during injection molding.

### **The introduction of the new measuring method**

The new measurement procedure uses two steps to provide accurate information about the pvT properties of the polymeric materials. In the first step the specific volume of the melt is measured at different pressure levels in the injection unit of the injection molding machine, in the temperature range above  $T_g$ . In the second step the characteristics of the range below  $T_g$  (which largely depend on the processing parameters) are measured using a special mold.

The injection units of today's commercially available injection molding machines are precision machined with low tolerances and are therefore theoretically able to perform pvT measurements in the temperature range above  $T_g$ . In spite of this, none of the published measurements made in the injection unit were acceptably accurate, especially at higher pressures. Since at lower pressures conventional measurements and measurements made in the injection unit yielded very similar results, we have concluded that most measurement errors can be attributed to the neglecting of elastic deformations. Other possible sources of error in pvT measurements are the expansion of certain parts of the injection unit due to heat, the mechanical work done on the melt, the amount of melt in the nozzle, and possible inaccuracies of the displacement measurement system of the machine, which were also not mentioned in the publications. We performed compensation for the errors, which was always based on physical foundations.

During measurement thermal expansion increases the size of both the injection unit and the screw both radially and axially. In an ideal case there is no error because the lengths of the cylinder and the screw are close to identical and axial expansion is therefore roughly the same. However, the temperature distributions of the cylinder and the screw are not equal because after plastication, the screw is only partially within the heated cylinder. Since the temperature distribution of the screw cannot be measured, the change in size was calculated using the volumetric thermal expansion coefficient of steel [21]:

$$V_{T_2} \cong V_{T_1} \cdot [1 + 3 \cdot \alpha \cdot (T_2 - T_1)], \quad (1)$$

where  $V_{T_2}$  [cm<sup>3</sup>] is the volume compensated for thermal expansion at the measurement temperature,  $V_{T_1}$  [cm<sup>3</sup>] is the volume at room temperature, indicated by the machine,  $\alpha$  [1/K] is the linear thermal expansion coefficient for steel,  $T_2$  [°C] is the measurement temperature, and  $T_1$  [°C] is room temperature.

During measurement elastic deformation occurs in both the cylinder and the screw. The highest degree of deformation occurs in the screw in axial direction, which can be well approximated by Hooke's law if the screw is considered a solid rod.

$$\Delta l = l \cdot \frac{\sigma}{E}, \quad (2)$$

where  $\Delta l$  [mm] is the change of length of the screw,  $l$  [mm] is the total length of the screw,  $\sigma$  [Pa] is the normal stress arising in the screw,  $E$  [Pa] is the elastic modulus of the material of the screw. During the compression of the plasticized melt, the pressure from it acts at the nominal cross sectional area of the screw (major diameter). The force from the pressure is uniform along the screw length, but the thread-grooves decrease the cross section of the screw (minor diameter), thus the normal stress in this section is higher. It was calculated that the screw can be modeled as a prismatic rod, with a 10% smaller cross section, which was proved with FEM analysis based on the real screw design. Linear deformation of the cylinder was neglected as although the same force is exerted on the cylinder as on the screw, the cross section of the cylinder is significantly larger, therefore the resulting deformation is an order of magnitude smaller. The injection unit also suffers radial deformation as a result of the hydrostatic pressure inside it. Since the cylinder module can be considered a thick-walled tube, the change in diameter can be calculated with equation (3) [22]:

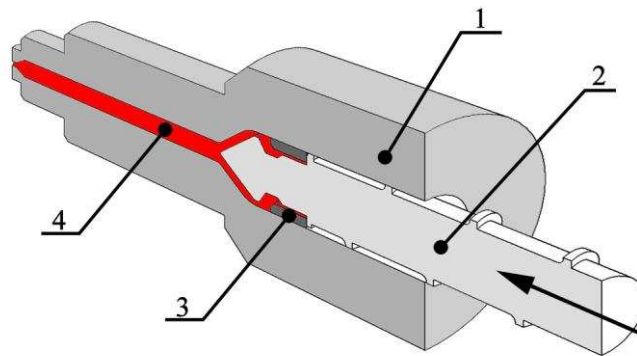
$$\Delta d = d \cdot p \cdot \frac{1}{E} \cdot \left( \frac{1 + \left(\frac{d}{D}\right)^2}{1 - \left(\frac{d}{D}\right)^2} + \frac{1}{\nu} \right), \quad (3)$$

where  $\Delta d$  [mm] is the change in diameter,  $d$  [mm] is the inner diameter of the injection unit,  $D$  [mm] is the outer diameter of the injection unit,  $p$  [Pa] is the inside pressure,  $E$  [Pa] is the Young's modulus of the material of the injection unit,  $\nu$  [-] is the Poisson's ratio of the material of the cylinder module.

When pressure is exerted on the melt, its temperature increases as a result of the mechanical work that was done on it. If pressure is exerted and measuring is done in a short time, the melt can only transfer little heat to the wall of the injection unit so the system can be considered close to adiabatic. In an adiabatic system the temperature change caused by pressure increase can be calculated with equation (4) [23]:

$$\left( \frac{\partial T}{\partial p} \right) = \frac{\alpha \cdot T \cdot v}{c_p} = \frac{\alpha \cdot T}{\rho \cdot c_p}, \quad (4)$$

where  $\partial T$  [K] is the temperature change,  $\partial p$  [Pa] is the pressure change,  $\alpha$  [1/K] is the thermal expansion coefficient,  $\rho$  [kg/m<sup>3</sup>] is the density,  $v$  [m<sup>3</sup>/kg] is the specific volume, and  $c_p$  [J/kgK] is the specific heat. The screw of the injection molding machine cannot force out all the melt accumulated in front of it, based on the construction of the screw-tip and the non-return valve (Fig. 1).



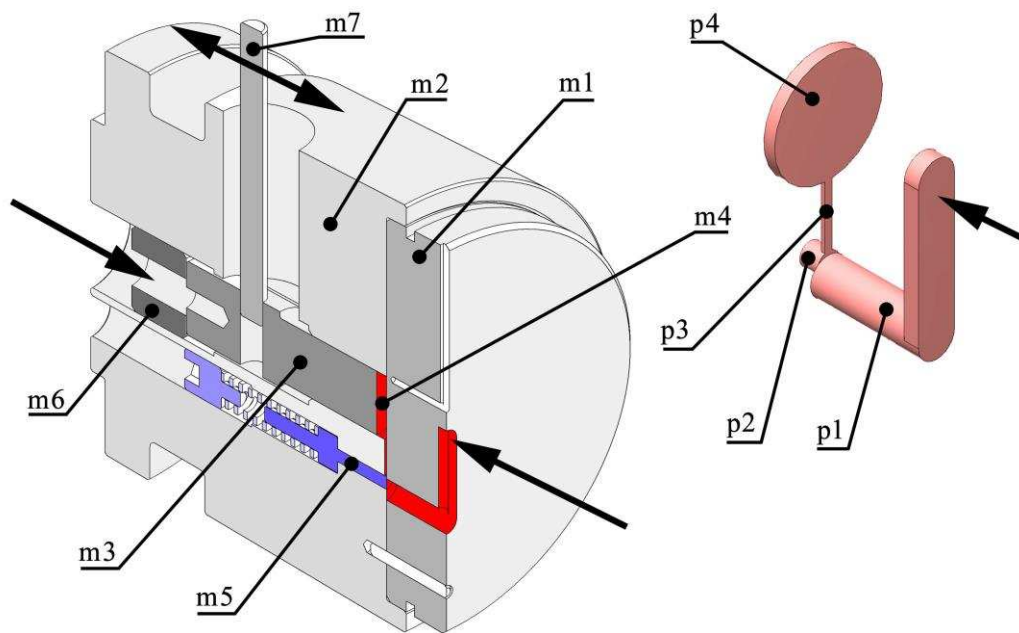
**1. Figure Definition of the “dead spot” (1—barrel and the nozzle, 2—screw, 3—non-return valve, 4—dead spot). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]**

The material in this "dead spot" is also compressed although it hasn't been taken into consideration by the machine. If the material in the dead spot is neglected during the measurement, the melt seems to be more compressible than it is. In order to eliminate the error, the size of the dead spot was determined and in calculating the volume change during the compression of the melt, the whole amount of melt (including the dead spot) was used.

The compensated specific volume measured with the nozzle blocked was used when calculating the specific volumes measurable at temperatures below  $T_g$ , and to describe the  $p$  $v$  $T$  properties of the investigated resins above temperature  $T_g$ , where they are independent of processing technology.

The second step of the new  $p$  $v$  $T$  measurement method makes it feasible to measure the  $p$  $v$  $T$  properties of the polymer in the temperature range below  $T_g$  under conditions identical to conditions in the injection molding process. During injection molding the hot polymer melt injected into the mold gets to the cold wall of the mold, and cools down as a result. When the polymer cools, its volume and consequently its specific volume changes. The second step of the new measurement method makes it possible to determine the specific volume by continuously monitoring the volume change of the melt cooling in the mold. To test the procedure, we have developed a special mold, which differs from conventional molds in several respects. The two most significant differences are that the size of the mold cavity can be continuously changed with a movable core, and the gate can be blocked to stop the melt going through it. The gate needs to be closed because, similarly to other  $p$  $v$  $T$  measurement methods, it has to be ensured that the material cannot leak from the cavity, which in this case is the measuring chamber, therefore the mass of the sample remains the same throughout the measuring process. The structure of the mold can be seen in Fig. 2.





**2. Figure** The layout of the pvT measurement device (m1—inlet plate, m2—mold base, m3—movable core, m4—measuring chamber, m5—spring-actuated non-return valve, m6—sample thickness limiter, m7—thickness measuring rod, p1—part inlet, p2—lockable gate, p3—gate, p4—part for the measurement). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The measurement process starts with the closing of the mold and injecting the melt. After injection, the melt fills the sprue and the runner, then the cavity, after a spring valve opens. After the cavity is filled, pressure is no longer needed so the pressure of the system decreases and the non-return valve stops the melt from flowing backwards.

One wall of the cavity is a core connected to the ejection system of the injection molding machine. This core is movable throughout the whole process, and the pressure in the cavity can be regulated with its movement during the whole measurement. The volume change of the cavity can be calculated from the displacement of the core, and the average specific volume can be calculated based on the mass of the sample. After the spring valve closes, the ejection system of the injection molding machine creates the right pressure in the cavity. When the desired pressure is reached, the measurement process can start, during which the continuous movement of the piston follows the volume change of the sample until it is completely cooled.

Since polymers have low thermal conductivity, and there is a considerable difference between the temperature of the melt injected into the mold and the temperature of the wall of the mold, the temperature difference between the inside and outside of the part can reach more than 100°C during cooling. This temperature distribution, which also continuously changes throughout the measuring process cannot be neglected, therefore the measured time-core displacement curve cannot be used directly to calculate the specific volume, because compensation is necessary. To do this, the temperature distribution of the sample throughout the whole measuring process is required, which can be well approximated with simulation or analytically. Further compensation may be necessary because of the thermal expansion or the volume change of the measuring chamber due to heat. As these factors are expected to cause errors several orders of magnitude smaller than the temperature distribution of the sample, they were neglected during measurements. Pressure was calculated as the ratio of the force applied to the piston and the cross-sectional area of the piston – friction was neglected. The measurements were started by the injection molding of cylindrical samples of a diameter of 30 mm and an initial height of 3 mm. The pressure achievable with the new method depends on the ejection system of the injection molding machine. The machine we used was able to reach a maximum pressure of 28 MPa.

A two-dimensional thermodynamic model was used to calculate the temperature distribution of the sample. This means that it was assumed that the sample does not give off heat on the cylinder wall, therefore the isotherms are parallel to the base of the cylinder. The differential equation of thermal conduction was solved with the explicit approximation method. Since amorphous polymers do not produce heat during cooling, the following equation was used for the calculations:

$$\frac{t(x, \tau + \Delta\tau) - t(x, \tau)}{\Delta\tau} = a \cdot \frac{t(x + \Delta x, \tau) + t(x - \Delta x, \tau) - 2 \cdot t(x, \tau)}{\Delta x^2}, \quad (5)$$

where  $t$  [°C] is the temperature,  $\tau$  [s] is the time,  $x$  [m] is the location, and  $a$  [m<sup>2</sup>/s] is the thermal diffusivity. As a starting point it was considered that the temperature of the sample is identical throughout the whole cross-section, and the cooling effect during the filling and the shear heating effect were neglected. In calculating the temperature distribution the sample was considered as  $k$  disks, in which temperature was assumed the same all over. The mass in each cell was assumed to remain the same throughout the measurement process and it was assumed that only the thickness of each disk changes. The total thickness of the sample is the sum of the thicknesses of each disk. The specific volume of each segment, which depends on

pressure and temperature and several other parameters is directly related to the thickness of the given segment.

$$s^{t_n} = \sum_1^k s_i^{t_n} = \sum_1^k \frac{v_i^{t_n}(p, T, \dots) \cdot \frac{m}{k}}{r^2 \cdot \pi}, \quad (6)$$

where  $s^{t_n}$  [m] is the total thickness of the sample at time  $t_n$ ,  $s_i^{t_n}$  [m] is the thickness of the given segment at time  $t_n$ ,  $v_i^{t_n}$  [m<sup>3</sup>/kg] is the specific volume of the given segment at time  $t_n$ ,  $m$  [kg] is the mass of the sample,  $k$  [-] is the number of all the segments,  $r$  [m] is the radius of the sample. The change of specific volume was described on isobars and the pressure-dependent parts of the 2-domain Tait equation were neglected. Data fitting to the individual isobars was done in two steps. In the first step the part above  $T_g$ , which is characteristic of melt state, was fitted based on the measurements in the injection unit of the machine. This ensures that the approximations of the model used do not adversely affect the calculation of the specific volume which is measured in melt state above  $T_g$  and is independent of technology. In the second step of data fitting the parameters of the 2-domain Tait equation were optimized with global data fitting to match the measured sample thicknesses and the thicknesses calculated with the model as closely as possible throughout the whole time of the measurement process. In this step the glass transition temperature is determined along with the specific volumes in the range below  $T_g$ .

## Materials and equipment

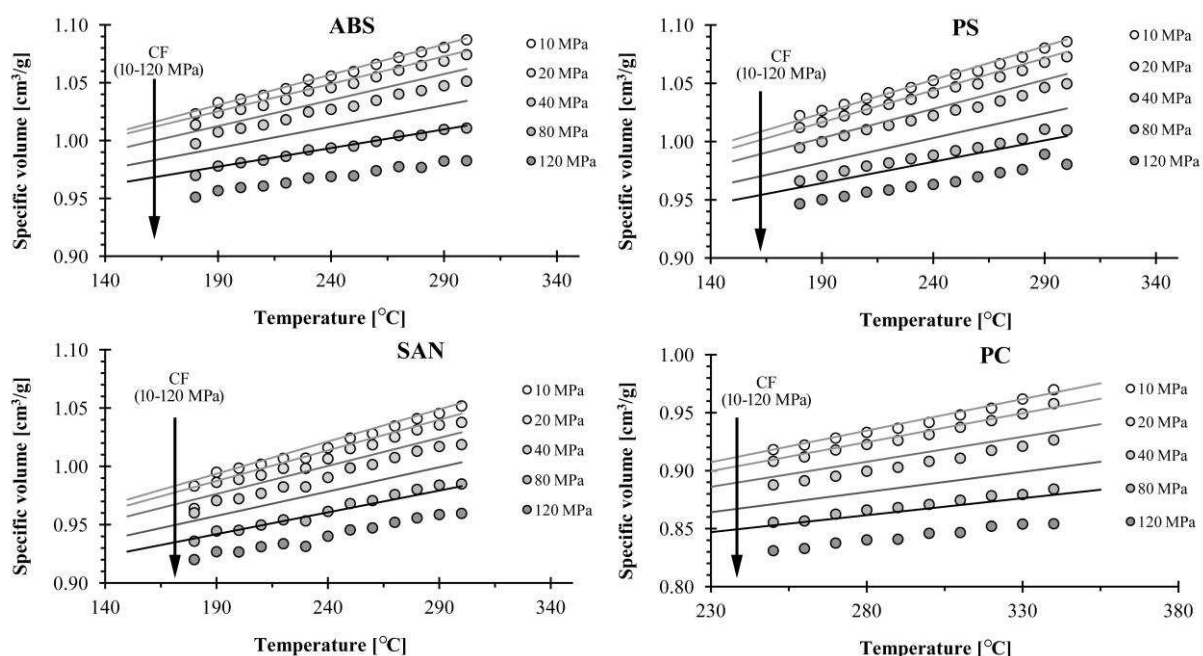
Measurements were made on amorphous polymers. The materials used were BASF Terluran GP-35 type ABS, BASF Polystyrol 143E type PS, Sabic Lexan 915R type PC, and BASF Styrolution Luran 368R type SAN. Specific heat was measured with TA Instruments Q2000 type DSC equipment, thermal conductivity was determined at 55°C with the hot plate method. The pvT measurements were performed on an Arburg Allrounder 370S 700-290 Advance injection molding machine. Mold temperature was 25°C in all cases, the temperature of the melt varied according to the materials but it was always near the maximum processing temperature recommended by the manufacturer. The fill time of the mold varied between 0.6 and 0.8 seconds depending on the polymer. During the measurement the displacement of the core was measured with an accuracy of 0.001 mm. The mass of the samples was measured with an Ohaus Explorer scale with an accuracy of 0.1 mg. To validate the novel measuring method and equipment, pvT tests were performed using indirect dilatometry. The tests were performed in isobar cooling mode, the cooling rate was 5°C/min. In the case of ABS, PS and

SAN, the measurements were made in the 30-300°C range, and with PC in the 30-340°C range.

## Results and evaluation

The measurements in the range above  $T_g$  were carried out while the nozzle was blocked, as published in several studies, in the 7-120 MPa pressure range. In the case of ABS, PS and SAN, the measurements were made in the 180-300°C range, and with PC in the 250-340°C range, with steps of 10°C. To avoid the uncertainty caused by the delay of the non-return valve, the screw was moved forward before the measurements. The possible leakage has been analyzed for all the four different materials at the highest temperature and pressure. It was proved that the screw has not moved further advance thus there were no leakage during the measurements.

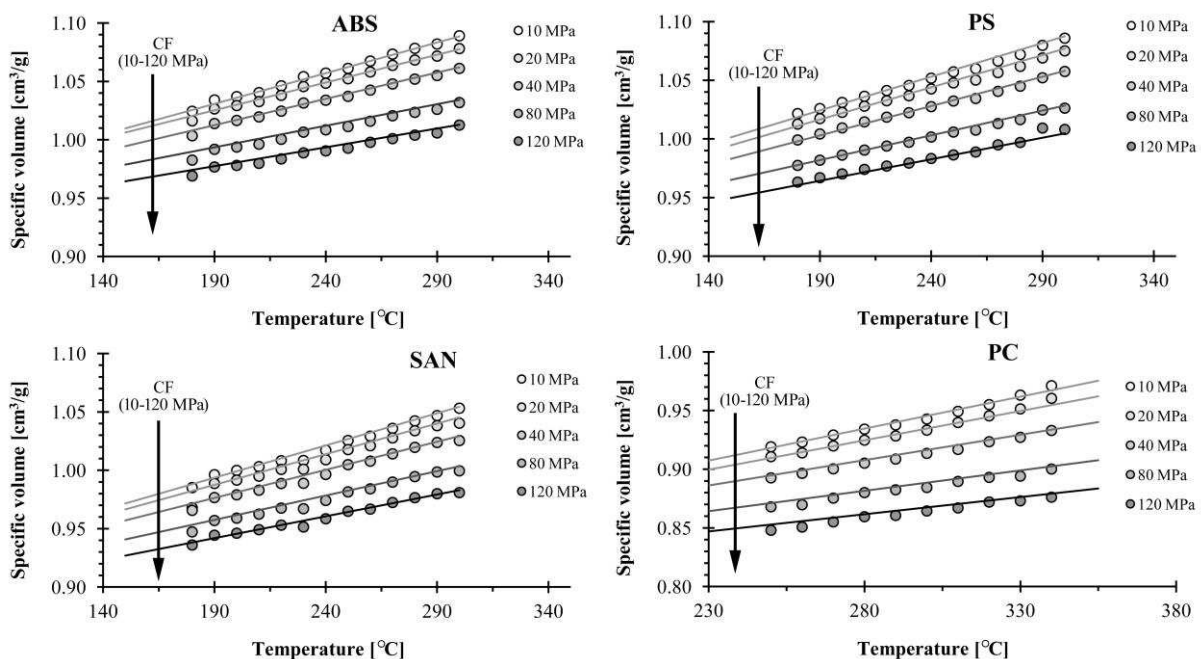
Linear equations were fitted on the data points measured for the individual isobars to eliminate the small errors caused by the slight fluctuation of the data. The data fitting was performed with least square regression. The  $R^2$  values for the different isobars were 0.989-0.995 for the ABS, 0.975-0.996 for the PS, 0.970-0.988 for the SAN and 0.988-0.996 for the PC. Fig. 3 shows the data points measured with the different polymers, and the fitted curves without compensation, compared to the data measured with the Confining Fluid technique.



3. Figure The results of the measurements in the range above  $T_g$  without compensation compared to the results of the confining fluid (CF) method.

As can be seen, according to the data published in the literature [24], there is a considerable difference between the results measured at higher pressures. The compressibility of the samples appeared higher than in the case of the Confining Fluid measurement for each polymer. The largest difference can be observed with the ABS sample, here the difference of the values measured at 1200 bar and 300°C was 0.035 cm<sup>3</sup>/g, meaning that the error was less than 3.6% in all cases.

The dead spot before the screw of the injection molding machine was 17 cm<sup>3</sup>, which causes a considerable error in compressibility measurements even with the maximum stroke. Since compressibility increases with temperature, the error experienced at higher temperatures is also larger, which causes an apparent decrease of the thermal expansion coefficient. The error resulting from the dead spot before the screw was about 1.6% in case of the maximal applied temperature and pressure. The second highest error comes from thermal expansion, which was 0.9 cm<sup>3</sup> at the maximum stroke and the maximum temperature. This can cause 0.85% difference in the results if thermal expansion is not taken into consideration. The error resulting from the elastic deformation of the screw was considerably less. The length of the screw is about 800 mm, which contracts a maximum of 0.5 mm at the 120 MPa injection pressure causing 0.45% error. The errors were significantly reduced with the performed compensation (Fig. 4).

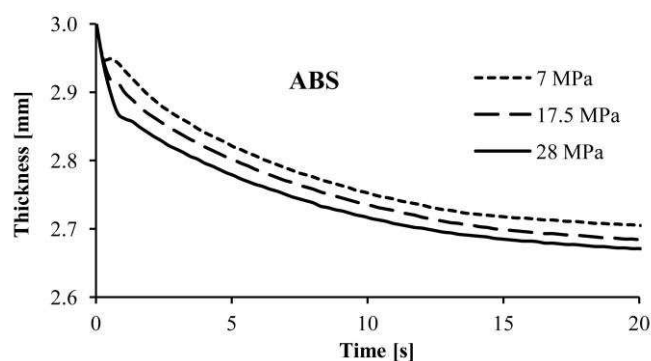


**4. Figure** The results of the measurements made in the range above T<sub>g</sub> after compensation, compared to the results of the confining fluid (CF) measurement procedure.

The maximum difference to the Confining Fluid technique in the pressure and temperature range used went under 0.2% in the case of all investigated polymers. The difference between

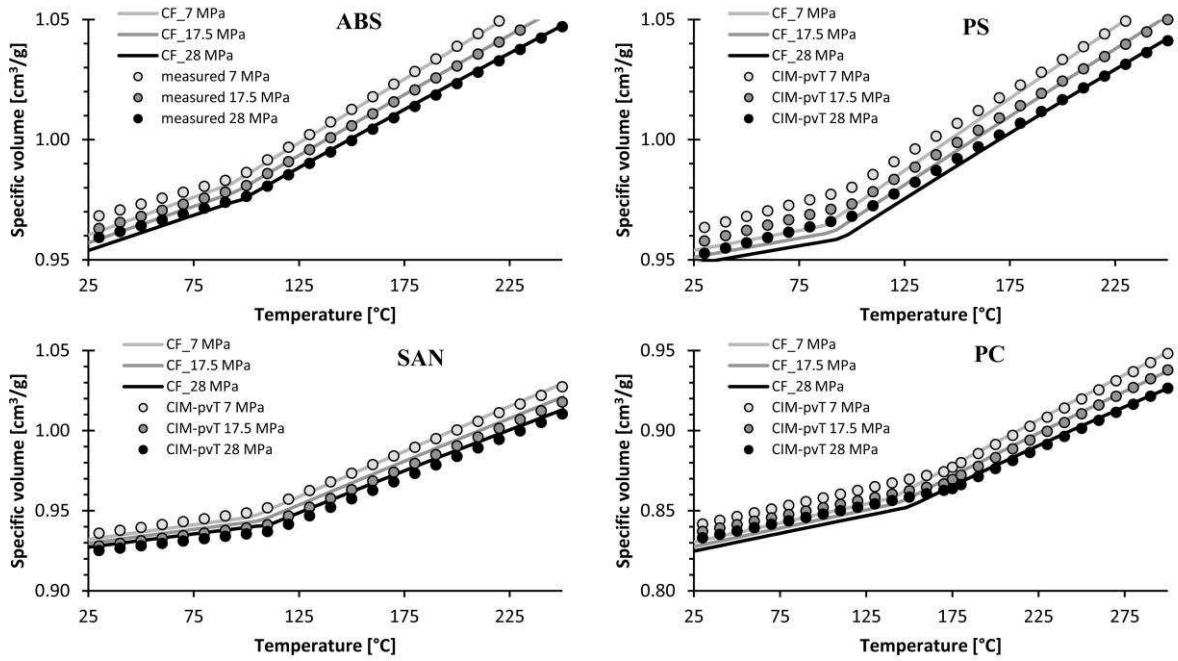
the data measured in the injection unit and with the Confining Fluid method can probably be attributed to slight fluctuations in the manufacturing technology of the polymers or the change in molecular weight occurring during the Confining Fluid procedure. The advantage of measurement in the injection unit is that measurement takes only a short time and in that short time most polymers suffer practically no degradation.

In the second step of measurement the range of  $T_g$  and below was measured with the special injection mold. Measurements in the mold were made with isobaric cooling, which best approximates the processes during injection molding. When filling the mold the temperature of the melt was set  $10^\circ\text{C}$  lower than the allowed maximum temperature with the given polymer so that the mold could be filled using relatively low pressure. Fig. 5 displays the change of thickness of the ABS sample as a function of time at a pressures of 7, 17.5 and 28 MPa. It can be seen that after filling the buildup of pressure took about 1 sec, therefore the initial, transient part of the curves were neglected in the evaluation process.



5. Figure The change of thickness of the ABS sample as a function of time at 28 MPa.

The reproducibility of the measured time-thickness curves proved to be good, the deviation of the measured curves from each other never exceeded 0.03 mm. The specific volumes for the temperature range below  $T_g$  were determined using the time-thickness curves, the temperature distribution and the specific volume data for the temperature range above  $T_g$ . The cooling rate is different at every point of the sample, which influences the specific volume at the given point. This effect was neglected during evaluation, therefore the measured values can be considered average values at the sample thickness and cooling conditions used. The values measured with the new method at 7, 17.5 and 28 MPa compared with the values measured using the Confining Fluid technique can be found in Fig. 6.



6. Figure Data measured with PS and SAN (a/b), and data measured with ABS and PC (c/d).

The data obtained with the new procedure represent the usual behavior of amorphous polymers. The  $T_g$  temperatures shown by the curves shifted towards higher temperatures compared to values measured with the conventional method due to the considerably higher cooling rate. Specific volumes in the range below  $T_g$  were always higher than those measured with the Confining Fluid procedure, which can also be attributed to the higher cooling rate. In the case of the 3 mm nominal thickness samples the cooling rate near  $T_g$  was 90 °C/min, which may vary widely according to the thickness of the sample and the technological parameters.

Cooling rates in parts near and further away from the mold wall differ considerably. Since both  $T_g$  and the specific volume under  $T_g$  are a function of the cooling rate, the calculated values can be considered as an average depending on the technological parameters and wall thickness used.

The pressure dependence of the  $T_g$  values measured with the new procedure are quite similar to the values obtained with the Confining Fluid procedure, in spite of the relatively narrow pressure range used. The pressure dependence of the transition temperature was around  $2.8 \cdot 10^{-7}$  K/Pa in the case of styrene-based polymers, whereas in the case of the examined polycarbonate it was  $4.2 \cdot 10^{-7}$  K/Pa. The cooling rate-dependence of the transition temperature may vary widely, but with most polymers it can be estimated with the constants of the WLF equation ( $\theta = C_2/C_1 = 51.6/17.44 = 3$ ) quite well. Kovács et. al. [25] found that the connection between the shift in  $T_g$  and the change in cooling rate shows a logarithmic relationship:

$$\Delta T_g = \theta \cdot \log(q/q_0), \quad (7)$$

where  $\Delta T_g$  is the shift in the glass transition temperature,  $\theta$  is a constant characteristic of the material and  $q$  and  $q_0$  are cooling rates, thus the experienced 3-4°C shift in  $T_g$  compared to the Confining Fluid procedure can be considered valid since the cooling rate was about an order of magnitude higher in the case of the new procedure. With appropriate thermal modeling, the new method can also be used to measure the pvT properties of semicrystalline materials.

## **Conclusion**

A new measurement procedure was developed, enabling to measure the pvT properties of thermoplastic polymers during injection molding with isobaric cooling, under the thermal conditions of injection molding. To achieve the desired accuracy, compensations were performed. A special mold was developed and thermal modeling was used to measure the solid phase. It was proved that the newly developed method works by measuring the pvT properties of ABS, PS, SAN and PC materials in the pressure range between 7-28 MPa. The measured data correlate well above the transition temperature with data measured with the Confining Fluid procedure. The specific volume under the transition temperature (characteristic of real injection molded products) was determined at considerably higher cooling rates than are used with the Confining Fluid procedure. The pressure dependence of the transition range and its shift due to the significantly higher cooling rate correlates well with data in the literature.

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