Effect of Cooling Rate and Shear-Induced Crystallization on the Pressure–Specific Volume–Temperature Diagram of Isotactic Polypropylene

E. FLEISCHMANN and J. KOPPELMANN, *Institut für Werkstoffkunde und -Prüfung der Kunststoffe, Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria*

Synopsis

Rectangular plates were injection molded with isotactic polypropylene. At a pressure of 1300 bar the mold was sealed mechanically in the gate. After the injection and compression phase the internal pressure decay has been calculated using the pressure–specific volume–temperature diagram and compared with measurements. The calculation method is described. The pvT diagram determined on stationary melt at a low cooling rate yields no good approximations of the measured values. It is shown which modifications of the pvT diagram are necessary to obtain a better description of the melt behavior under injection molding conditions. At the end of the cooling phase, the calculated pressure differs from the measured pressure. The reason is the volume change of the mold caused by the high internal pressure.

INTRODUCTION

At the processing of semicrystalline or amorphous polymers, pressure–specific volume–temperature (pvT) diagrams proved to be very useful for the optimal process control.[1-3] The pvT diagrams given in the literature[4] are usually measured on stationary melts at relatively low cooling rates.[5] But at injection molding high shear rates and high cooling rates occur. Besides, particularly at injection molding with mechanical sealing, high pressures are applied. These processing conditions strongly affect the specific volume. Thus, injection molding processes cannot be described correctly by these diagrams.

In a previous paper[6] it was shown that at injection molding the actual behavior of a broad molecular weight distributed polypropylene (PP) grade is insufficiently described by the pvT diagram recorded at a low cooling rate. By means of this diagram pressure decays are calculated in the mold mechanically sealed in the gate. Considerable deviations from measured values were found and corrected by modifying the pvT diagram.

In this work the calculation method is tested on a small molecular weight distributed polypropylene compound. To compare the results with former ones,[6] the same injection molding conditions are used. It is of special interest to know if the calculation method also fits in this case, since, in contrast to the former experiment,[6] a residual pressure exists at the end of the cooling phase. The influence of polymer structure, cooling rate, and pressure on the pvT behavior and, consequently, on the course of the internal pressure curves is studied.

EXPERIMENTAL

Materials

For the present investigation a commercial isotactic polypropylene Daplen PT 55 [MFI (230°C/21.19 N) = 18.6 g/10 min, M_w/M_n = 2.5] was supplied by Petrochemie Danubia, Austria. This polypropylene grade exhibits almost the same rheological behavior[7] at injection molding conditions as the product grade Daplen KS 10 [MFI (230°C/21.19 N) = 8.0 g/10 min, M_w/M_n = 5.7] used in one of our papers.[6] However, owing to the different molecular parameters the zero shear viscosity is smaller[8] by a factor of 8 in the case of PT 55 than with KS 10. The ratio of the relaxation times is of the same order.

In Figure 1 the specific volume as a function of temperature illustrates the different behavior of the two polypropylene grades at three different pressures. The curves were measured at a cooling rate of 0.4 K/s.

Injection Molding

An injection molding machine Model ES 250 manufactured by Engel, Austria, was used. A rectangular plate (230 × 70 × 2 mm³) with film gate was molded using injection parameters as follows: melt temperature 200°C, mold temperature 20°C, flow front velocity 100 mm/s. The internal pressures measured at the begin (near the gate) and at the end (remote from the gate) of the flow path are shown as a function of time in Figure 2.

At the maximum mold internal pressure of 1300 bar, the mold was mechanically sealed in the gate. Additionally, in Figure 2 the pressure curves of the
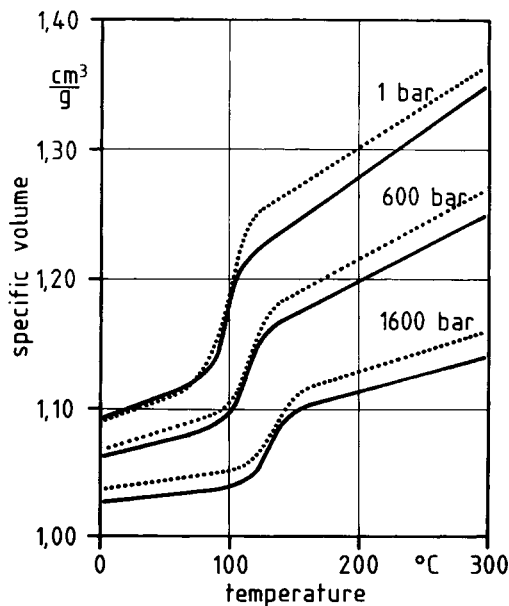

Fig. 1. pvT diagram for PP–PT 55 (——) and PP–KS 10 (· · ·) measured at an average cooling rate of 0.4 K/s at pressures of 1, 600, and 1600 bar.
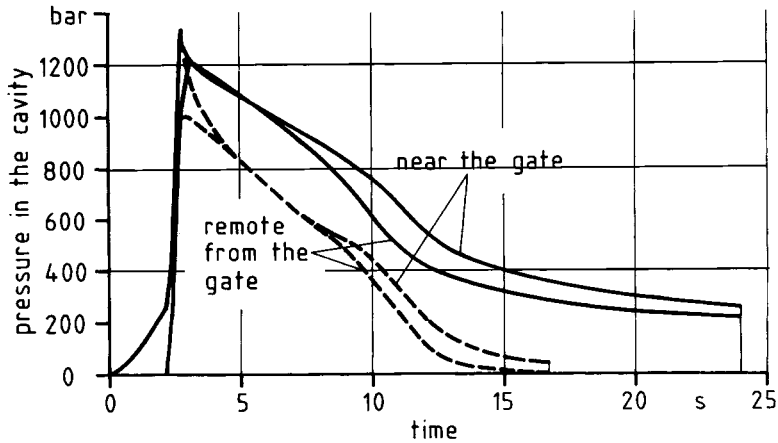
Fig. 2.   Internal pressure curves near and remote from the gate for PP–PT 55 (———) and KS 10 (– – –), respectively.

corresponding experiment with KS 10 are also drawn.[6] In both experiments an internal maximum pressure of 1300 bar was applied; but in the case of KS 10 the pressure equalization in the cavity needs 2.4 s whereas in the case of PT 55 only 0.3 s is necessary. The reason of this difference is the longer relaxation times of KS 10. Further, at the experiment with PT 55 a residual pressure of 240 bar occurs at the end of the cooling stage.

RESULTS AND DISCUSSION

Figure 3 shows the thickness of the highly oriented surface layer along the flow path determined using a polarizing microscope (Leitz, FRG). At a flow length greater than 180 mm, no surface layer thickness can be measured. An average layer thickness of 0.28 mm is concluded. Assuming a symmetrical filling
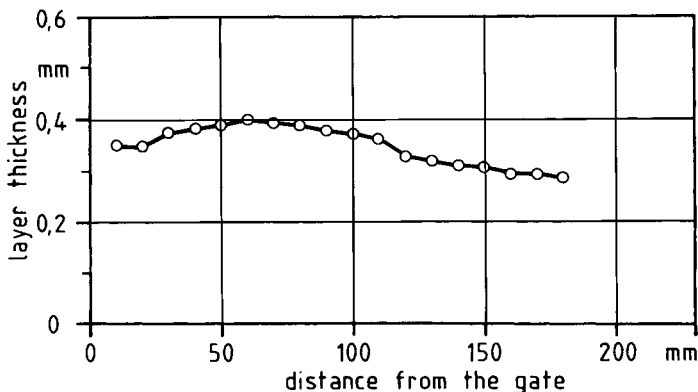

Fig. 3.   Surface layer thickness as a function of the distance from the gate for a plate of PP–PT 55 injection-molded with mechanical sealing (melt temperature 200°C, wall temperature 20°C, flow front velocity 100 mm/s, maximum pressure 1300 bar).

and cooling behavior, only one half of the plate is taken for the calculation of the pressure decays in the mold. Hence, the plate thickness can be divided into a core zone of 0.72 mm thickness and a surface zone of 0.28 mm thickness. The highly oriented outer zone is formed, caused by shear flow in the injection phase[9] whereas no orientation occurs in the core zone at injection molding with mechanical sealing.[10]

In Figure 4 the pvT diagram of PP–PT 55 measured at an average cooling rate of 0.4 K/s is given. The description of the points 1–6 is explained as follows: From the injection time of 2.30 s for the mold between the two pressure transducers, an average residence time of the melt of about 1.15 s is concluded (cf. Fig. 2). The cooling of the melt is calculated from the analytical solution of the heat conduction equation ($a = 0.065$ mm^2/s). At the end of the filling stage, i.e., after 1.15 s, the average temperature of the plate is 138°C, the average temperatures of both the inner zone and the outer zone are 183 and 74°C, respectively. These temperatures and the averaged pressure of 125 bar yield points 1, 3, and 5 in the pvT diagram. At the end of the compression stage the corresponding points 2, 4, and 6 are calculated for an average cooling time of 1.65 s and a pressure of 1300 bar. In this consideration a compression time of 0.5 s is added to the average fill time and that pressure near the gate is taken when the mold is sealed mechanically (cf. Fig. 2).

Figure 5 shows calculated pressures in the cavity using in contrast to the method of Gissing and Knappe,[11] two zones and different assumptions of the pvT diagram. An example is given illustrating the way in which the pressure curves are calculated. Curve 1 corresponds to the measured pvT diagram of PT 55 shown in Figure 4. The isochoric cooling of the inner zone starts at point 4
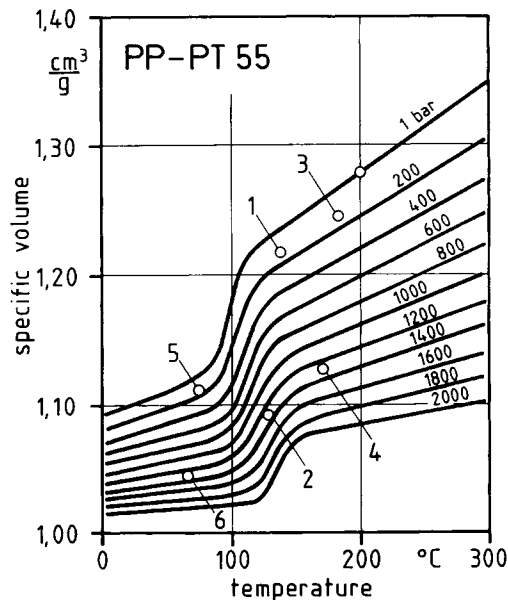

Fig. 4. pvT diagram for Daplen PT 55 measured at an average cooling rate of 0.4 K/s at pressures of 1, 600, and 1600 bar[5]; other pressures are interpolated or extrapolated; points 1–6, cf. text.
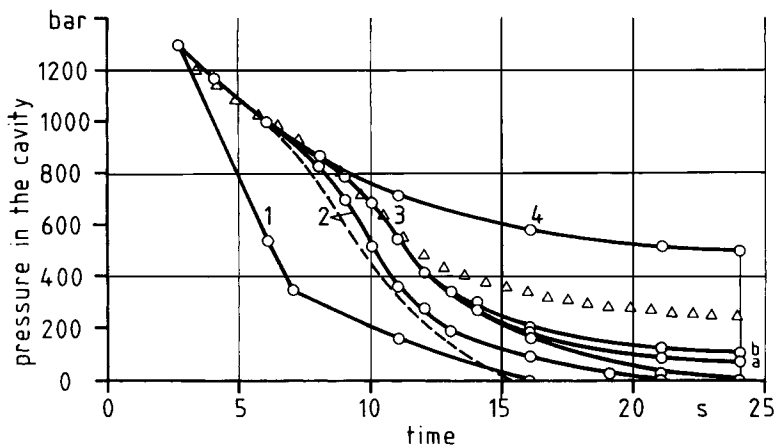
Fig. 5. Calculated pressure curves: 1, 2, 3, 3a, 3b, and 4 correspond to different assumptions of the pvT diagram of PP–PT 55 (cf. Fig. 6); curve 2 (- - -) relates analogously to the pvT diagram of PP–KS 10; ($\triangle\triangle$) measured averaged pressure curve.

($\rho_{sp} = 1.127$ cm^3/g) and that of the outer zone at point 6 ($\rho_{sp} = 1.045$ cm^3/g). The average specific volume of both zones is about 1.104 cm^3/g, for which the thicknesses of the zones are taken into account. During the cooling stage this average specific volume remains constant. Now the average temperatures in the inner and outer zone are calculated for a certain cooling time. The values of specific volumes corresponding to these temperatures are determined at different pressures and the pressure regarding to the average specific volume of 1.104 cm^3/g is estimated by interpolation. Consequently, repeated for more cooling times, curve 1 is obtained which deviates strongly from the measured curve (marked by symbol $\triangle$ in Fig. 5).

In our previous study,[6] it was demonstrated that better agreements between calculation and experiment are received if the pvT diagram is modified as shown for pressures of 1 and 1600 bar in Figure 6. The decrease of the specific volume where crystallization occurs is shifted to higher temperatures for the highly oriented outer layer (dashed curve in Fig. 6) and to lower temperatures for the inner layer (curves 2 and 3 in Fig. 6) showing little or no orientation. In this way shear-induced crystallization as well as supercooling effects are considered.

The calculation of the pressure curve in the cooling phase using curves 2 and 3 for the inner zone and in both cases the dashed curve in Figure 6 for the outer zone yields curves 2 and 3 in Figure 5. Curve 3 in Figure 5 gives a good approximation of the measured curve (marked by the symbol $\triangle$) up to a time of 12 s. After this time the deviation increases.

Better results are obtained shifting the specific volume in the solidified range towards higher values. It is well known that specific volume below the melting point increases with increasing cooling rate.[12] The crystallization is suppressed because the time available for crystal growth decreases due to the increased cooling rate. Thus the density is reduced and therefore the specific volume increases. The curves 3a and 3b result from a shift by about 1%. In curve 3b four zones are used instead of two. In this case a residual pressure of 110 bar is calculated at the end of the cooling phase. The neglect of the volume change
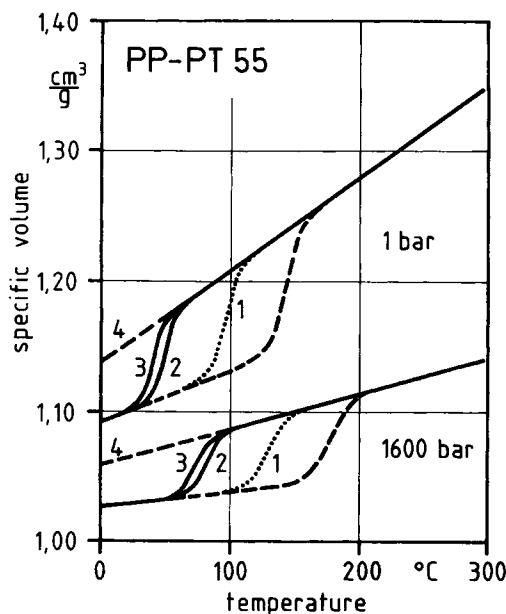
Fig. 6. Different modifications (curves 2, 3, and 4 and dashed curve) of the pvT diagram of PP–PT 55 shown at 1 and 1600 bar, measured curve 1 (· · ·).

of the mold caused by the high inner pressure is probably the main reason for the differences between measurement and calculation of the pressure curves in the cavity. Another reason is certainly due to the calculation of the temperature because heat friction, heat compression, and heat transfer in flow direction are not accounted.

In Figure 5 for the calculation of the dashed curve 2, the pvT diagram of PP–KS 10 was used.[6] The result reveals a strong dependence of specific volume on the polymer structure. With same conditions, relaxation times and molecular weight distribution determine the viscosity and the melt behavior. Curve 4 corresponds to the theoretical case that the inner zone solidifies amorphously without crystallization (cf. curve 4 in Fig. 6).

Further calculations were made to determine separately the pressure near the gate and remote from the gate (Fig. 7). Near the gate the thickness of the outer layer was chosen as 0.34 mm (cf. Fig. 3). The cooling time was about 2.7 s when the mold was sealed. The calculation occurred on the basis of assumption 3 of the pvT diagram (cf. Fig. 6). Remote from the gate the plate thickness was divided into two 0.5 mm thick layers. A cooling time of 0.6 s was determined up to mechanical sealing. For the outer layer assumption 2 of the pvT diagram and for the inner layer assumption 3 were applied (cf. Fig. 6). So different cooling rates were assumed in different distances from the surface of the plate. Of course, no equalization of pressure can be observed because the two calculations are decoupled.

CONCLUSIONS

This study has shown that the pvT diagram measured on stationary melt at low cooling rates must be considerably modified to get a satisfactory estimation
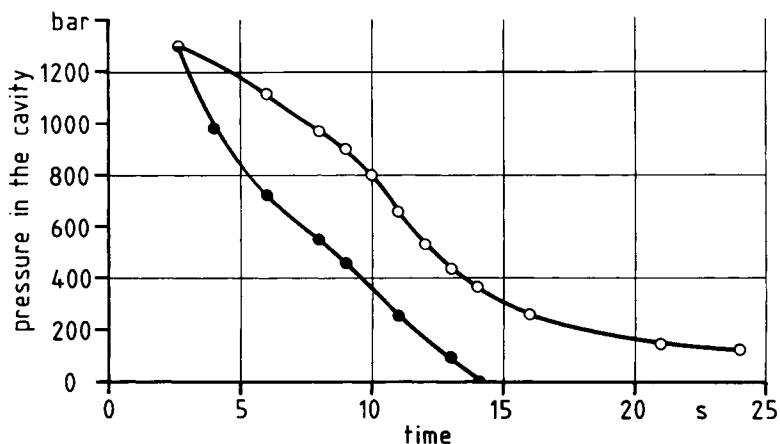
Fig. 7.   Calculated pressure curve near the gate (O — O) and remote from the gate (● — ●) for PP–PT 55 at injection molding with mechanical sealing.

of pressure curves during the cooling phase at injection molding with mechanical sealing in the gate. In addition to the corrections considering shear-induced crystallization affected by supercooling, in the solidified state a change of the pvT behavior is necessary owing to high cooling rates. It is expected that exact temperature calculations and the consideration of the volume change of the mold due to the high internal pressure will lead to a better agreement of calculated and measured pressure curves.

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