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Effect of pressure on the PVT behaviour of iPP as revealed by dilatometric measurements

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Summary

Isotactic Poly-propylene samples, previously prepared under known conditions of pressure and cooling rate by means of a special apparatus designed and set-up by the authors, were subjected to several isobaric runs at low cooling and heating rate in a confining fluid dilatometer (by GNOMIX). The effect of the previous thermo-mechanical histories and the effect of pressure in the dilatometry on specific volume of the samples was studied. Results show that the initial specific volume depends upon the previous thermo-mechanical histories, which however cancels out after the first heating run. Moreover the reported dilatometric experimental data support the evidence that an increase of pressure at a constant cooling rate acts as an increase of cooling rate at a constant pressure.

Introduction

Dilatometric measurements on polymeric materials represent a valuable source of information concerning their specific volume dependence upon the thermodynamic variables pressure and temperature, i.e. their Pressure-Volume-Temperature (PVT) behaviour. This outcome is of high scientific and technological relevance, since normal polymer transformation processes take place under elevated pressures (up to 100-200 MPa) and high cooling rates (up to hundreds of °C/s). Although the powerfulness of dilatometric apparatus is generally intrinsically constrained by the maximum achievable cooling rates (few °C/min), dilatometric studies can supply a significant contribution to the investigation of polymer solidification under processing conditions [1, 2]. The aim of this work is to highlight the effect of pressure on the specific volume of iPP samples prepared under various conditions of pressure and cooling rate by means of a special apparatus described elsewhere [3-6]. For this purpose several isobaric runs at low cooling and heating rate have been performed. Effect of the previous thermo-mechanical history on the resulting PVT curves was also analysed.

Experimental

Dilatometric measurements were performed with a confining fluid pressure dilatometer built by GNOMIX and operating at the Dipartimento of Chimica, Materiali e Ingegneria Chimica of Politecnico di Milano. Three samples of an iPP grade kindly supplied by Himont (M_n = 75100; M_w = 483000; M_w / M_n = 6.4) were analysed.

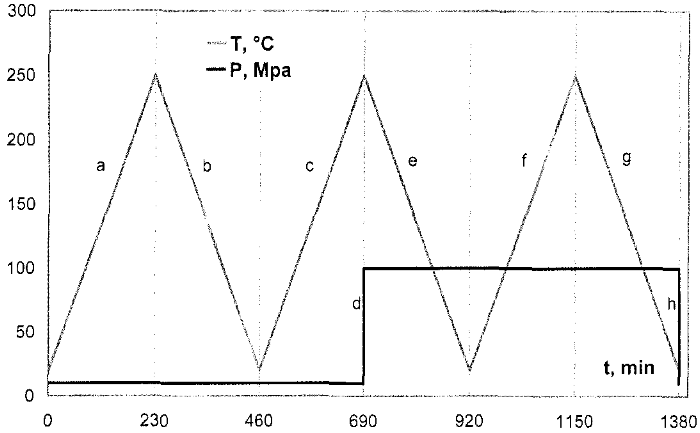

Fig. 1 Scheme of the PVT cycle.

Samples were prepared in a special apparatus described elsewhere [4-6] under known solidification pressures and cooling rates, which are reported in **Table 1** together with the density values measured (after preparation) at ambient pressure by a density gradient column. Samples (n° 1 to 3) were subjected to a PVT cycle consisting in 8 successive runs, as schematically indicated in **fig. 1**:

a) Isobaric heating at 10 MPa from room temperature to 210°C;
b) Isobaric cooling at 10 MPa from 210°C to room temperature;
c) Second isobaric heating at 10 MPa from room temperature to 210°C;
d) Isothermal compression at 210°C (in the molten state) from 10 MPa to 100 MPa (not reported on the following figures);
e) Isobaric cooling at 100 MPa from 210°C to room temperature;
f) Isobaric heating at 100 MPa from room temperature to 210°C;
g) Isobaric cooling at 100 MPa from 210°C to room temperature;
h) Isothermal expansion at room temperature (in the solid state) from 100 MPa to 10 MPa.

All isobaric runs both on heating (a, c, f) and on cooling (b, e, g), were performed at a constant rate of 1°C/min.

Table 1. Samples used for PVT measurement

Sample	Solidification pressure (MPa)	Specific volume (cm^3/g)	Cooling rate (°C/min)
1	0.1	1.1037	1
2	8	1.1130	30
3	24	1.1138	30

Results and discussion

Curves reporting specific volume as a function of temperature are shown in **figs. 2-4** with reference to samples n° 1, 2 and 3 indicated in **Table 1** respectively. Fig. 2 shows specific volume as a function of temperature in isobaric tests at two pressures (10 and 100 MPa) for sample n°1 (see **Table 1**) previously crystallized at ambient pressure and low cooling rate (1°C/min), this last value being the same as the cooling rate used in the experiments in the PVT apparatus.

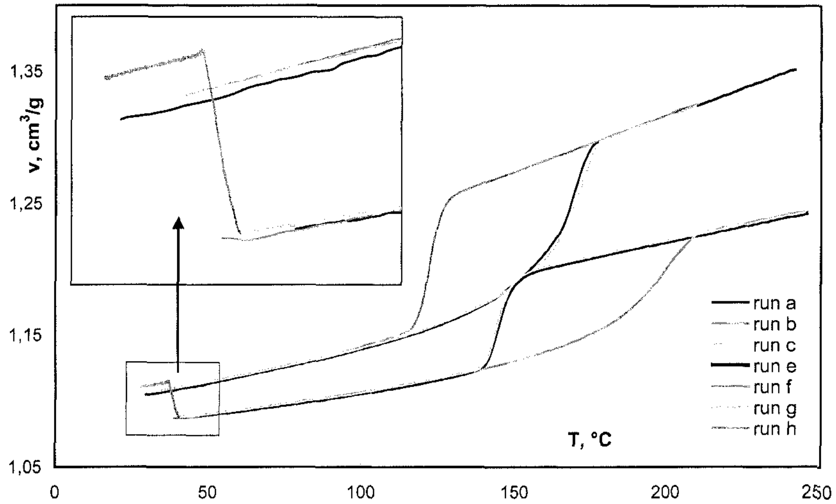

Fig. 2 PVT runs sample n° 1 (solidification conditions: 0.1 MPa and 1°C/min).

The starting point of curve a in fig. 1 represents the initial specific volume of the sample measured *in situ* (i.e. in the dilatometer) at the pressure at which the sample is held, i.e. 10 Mpa. After the isobaric melting run (run a) sample is solidified by a isobaric cooling run (run b), which brings the specific volume of the sample, at room temperature, to the same value exhibited by the sample at the beginning of the experiment (beginning of run a). This is basically related to the fact the sample had been previously crystallised at a cooling rate equal to the one at which was crystallised in the PVT (run b).

If we now consider **fig. 3** (sample n° 2, crystallised at 8 MPa and 30°C/min), it can be easily observed that the behaviour of this sample turns out to be quite different with respect to the previous one. As a matter of fact, the final specific volume value obtained in the end of run b (isobaric cooling at 10 MPa), is lower than the initial value exhibited by the sample at the beginning of run a.

This is due to the fact that sample n° 2, previously crystallised at a larger cooling rate than sample n° 1, is characterised by a lower density, i.e. by a larger specific volume, as indicated in **Table 1**. Melting and solidification runs (run a and b in **fig. 3** respectively) take place at a rate of 1°C/min, which leads to a final specific volume (end of run b in **fig. 3**) lower than the initial one (beginning of run a in **fig. 3**) for sample n° 2, while sample n° 1 did not show remarkable differences (see run a and b in **fig. 2**). Finally if we look at **fig. 4** (sample n° 3, crystallised at 24 MPa and 30°C/min), a behaviour similar to the one observed for sample n° 2 should be noticed (see **fig. 3**). In fact specific volume of sample n° 3 at the end of run b is lower than the one recorded at the beginning of run a, with a gap between the specific volume levels larger in **fig. 4** (sample n° 3) than in **fig. 3** (sample n° 2). This is related to the fact that sample n° 3 was previously crystallised at the same cooling rate as sample n° 2 (30°C/min) but at a larger pressure (24 MPa for sample n° 3 and 8 MPa for sample n° 2). Owing to the unusual behaviour of iPP elsewhere discussed [4-6], an increase of solidification pressure determines a decrease of final density (measured at ambient pressure after solidification): for this reason sample n° 3 is characterised by a lower density (i.e. by a higher specific volume) than sample n° 2, as reported in **Table 1**. Last but not least, the value of the specific volume recorded by the PVT at the end of run b is identical (in the limit of experimental error) for all the three samples, showing that the heating run b was able to cancel out the memory of previous thermo-mechanical histories. Indeed going back to **figs. 2-4** and looking at the isobaric cooling runs at 100 MPa (run e and g), we can notice that specific volume is not anymore affected by thermal cycles, i.e. for all samples runs g and e overlap. In other words, for what we discussed so far, the only remarkable differences between the three samples concern the comparison of runs a and b, as only the initial specific volume is affected by the previous thermo-mechanical history the samples underwent.

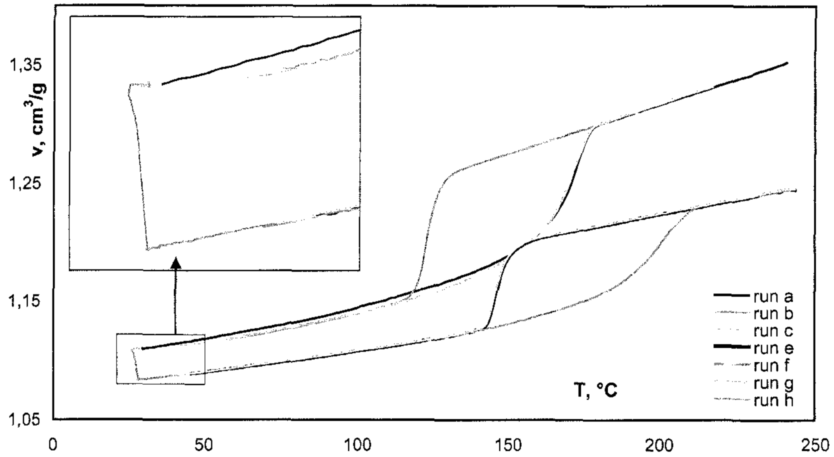

Fig. 3 PVT runs sample n° 2 (solidification conditions: 8 MPa and 30°C/min).

Table 2. Values of specific volumes (measured at 35°C) for samples 1 to 3 (see **Table 1**) after pressurization from atmospheric pressure up to 10 MPa (beginning of run a), after solidification at 10 MPa and 1°C/min (end of run b) and after solidification at 100 MPa and 1°C/min followed by a rapid depressurization to 10MPa (end of run h).

Sample	*Specific volume* (cm^3/g) Before run a	*Specific volume* (cm^3/g) After run b	*Specific volume* (cm^3/g) After run h
1	1.107	1.108	1.114
2	1.111	1.109	1.112
3	1.116	1.110	1.113

It may result interesting to compare specific volumes of samples crystallized as reported in **Table 1** and whith those of samples solidified at 100MPa in the PVT apparatus, as shown by run h, a rather vertical line in the V-T plots in **figs. 2** to **4**.

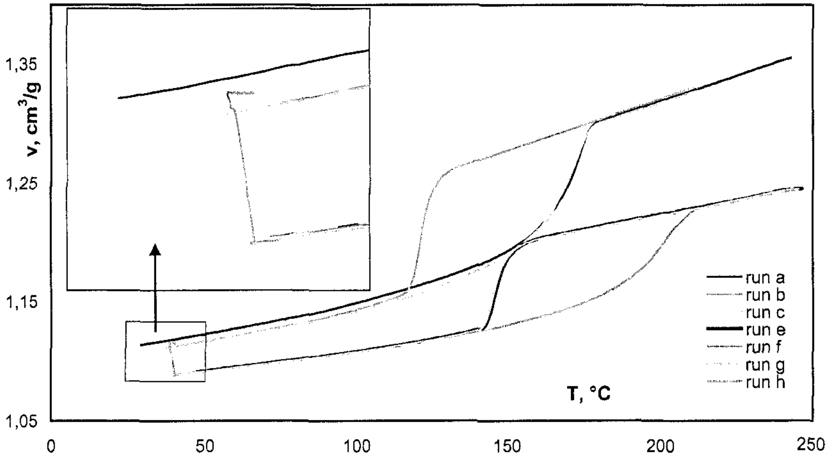

Fig. 4 PVT runs sample n° 3 (*solidification conditions*: 24 MPa *and* 30°C/*min*).

This comparison is reported in **Table 2**, which shows the specific volumes at 35°C of samples 1 to 3 after the pressurization from atmospheric pressure up to 10 MPa (beginning of run a), after solidification at 10 MPa and 1°C/min (end of run b) and after solidification at 100 MPa and 1°C/min followed by a rapid depressurization to 10MPa (end of run h). From this table it can be noticed that for all the considered samples the crystallization at 100MPa followed by a depressurization to 10 MPa produces a specific volume higher than that obtained by solidification at 10MPa. The observed pressure effect is peculiar for iPP, as observed by Zoller [1], and it is probably due to the decrease of the crystalline phase content on increasing pressure [3-6]. On the other hand, if specific volumes of sample 3 at the beginning of run a and at the end of run h are compared, it results that the volume is higher in the former condition. This could be due to the dominating effect of cooling rate, which is higher (30°C/min) in the crystallization at 24 MPa than in that (1°C/min) at 100MPa. Interestingly, if we consider sample two, the specific volumes before run a and after run h are similar, this suggesting a balancing between the pressure effect (higher for run h) and the cooling rate effect (higher for run a). More precisely, solidification at 8 MPa and 30°C/min leads to a specific volume (measured at 10 MPa) equal to the one determined by a solidification at 100 MPa and 1°C/min. In other words, an increase of solidification pressure from 10 to 100 MPa (at a cooling rate of 1°C/min) acts as an increase of cooling rate from 1 to 30 °C/min (at a pressure of 10 MPa). This observation, in agreement with what observed by the present authors [5-6] by alternative techniques, suggests a correlation between cooling rate and pressure, and thus the possibility of introducing a master curve approach to unify the pressure and cooling rate effects on the solidification of iPP.

Conclusions

In this work we considered the effects of crystallization pressure and cooling rate upon specific volume of iPP, as measured in the solid state at 10 MPa in a confining fluid high pressure dilatometer.

Comparison between specific volumes of samples crystallized at different pressures and/or cooling rates showed a density decrease with increasing cooling rate and pressure. While the increase of specific volume as cooling rate increases is the expected feature of semicrystalline polymers, the pressure effect is peculiar for iPP, as previously observed by Zoller [1] and elsewhere by the present authors [3-6].

Both the effects, already observable on considered samples before any treatment in the PVT apparatus, where confirmed by comparing initial specific volumes with those obtained by melting and crystallizing these samples at 10 MPa and 1°C/min in the pressure dilatometer.

On the other hand, PVT curves obtained after the first heating (indicated in this work as run a) showed a very good repeatability for all the three samples considered, this indicating that any previous thermo-mechanical history was erased in the melt phase.

Finally, the specific volume at 10 MPa of samples obtained by crystallization at 8 MPa and 30°C/min and at 100MPa and 1°C/min, respectively, are similar, and this corroborates the observation that an increase in pressure at constant cooling rate acts as an increase in cooling rate at constant pressure, thus supporting a master curve approach [5].

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Reference

[1] He J, Zoller P (1994) J. Polym. Sci., Part B: Polym. Phys., 32, 6:1049
[2] Termodinamik (1979) Carl Hanser Verlag Munchen Wien
[3] La Carrubba V (2001), PhD Thesis, CUES Ed. Salerno, ISBN: 88-87030-27-8
[4] Brucato V, La Carrubba V, Piccarolo S, Titomanlio G (2000) Int. Polym. Proc., 15, 1:103
[5] La Carrubba V, Brucato V, Piccarolo S (2000) Polym. Eng. And Sci., 40, 11:2430
[6] La Carrubba V, Brucato V, Piccarolo S (2002) J. of Polym. Sci., Part B: Polym. Phys., 40, 1:153