

The Pressure–Volume–Temperature Properties of Three Well-Characterized Low-Density Polyethylenes

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Synopsis

Pressure–volume–temperature relationships of three low-density polyethylenes are reported in the temperature range of 30°–225°C and in the pressure range of 0–2000 kg/cm². The same materials had previously been studied by the IUPAC Working Party on Structure and Properties of Commercial Polymers with regard to basic characterization, melt rheology, processing, and end use properties. They were found to be remarkably equal in basic parameters and in some of the melt rheology, but differences among the three samples were found in other rheological properties and in the processing and end use properties of blown film. We find the PVT relationships of these three samples to be practically identical. A numerical equation of state based on the Tait equation is established. It reproduces the measured specific volume data of the melts to better than 0.002 cm³/g.

INTRODUCTION

In 1975 the results of a collaborative study by the IUPAC Working Party on Structure and Properties of Commercial Polymers on basic parameters, melt rheology, processing, and end use properties of three very similar low-density polyethylenes were published.¹ The three samples, designated A, B, and C, were practically identical as tested by physical-chemical methods: they had equal densities of 0.919 ± 0.001 g/cm³ at 20°C, identical IR data as far as methyl and vinylidene groups were concerned, and also identical number-average molecular weights of $M_n \approx 20,000$. They differed apparently in their weight-average molecular weight M_w ($A \approx 6 \times 10^5$, $B \approx 8-9 \times 10^5$, $C > 10^6$) and in vinyl groups (B had definitely more vinyl groups than either A or C).

Rheological testing showed the linear viscoelastic behavior and the shear viscosity function $\eta(\dot{\gamma})$ to be practically identical for the three samples. Differences were found in the melt elasticity properties and the tensile behavior of the melt. Remarkable differences were also found in the behavior of these materials in the blown-film process and in the end use properties of blown films. For details regarding the results of all these tests the reader is referred to reference 1.

As a further characterization of the three samples A, B, and C, we thought it of interest to study the pressure–volume–temperature (PVT) relationships of these samples, both in the solid and in the molten state. Our aim was primarily to check if there were significant differences in the compressibility behavior; but it is, of course, also of inherent interest to have available precise data on the specific volume as a function of pressure and temperature for these unusually well-characterized samples.

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EXPERIMENTAL

The apparatus and evaluation procedure for obtaining PVT data have been described in detail.² The sample (about 1 g) is contained in a rigid sample cell one end of which is closed by a flexible metal bellows. The space in the cell not taken up by the sample is filled with mercury under vacuum. This sample cell is mounted in a pressure vessel, and pressures* to 2000 kg/cm² are applied with a hand pump, using silicone oil as the pressure-transmitting fluid. The applied pressure is transmitted to the contents of the sample cell by the bellows, which expands until the pressure in the sample cell equals the applied pressure. The displacement of the bellows is measured by a linear variable differential transformer the coil of which is mounted outside the pressure vessel. This displacement can be converted to a volume change of the polymer sample, making use of the cross-sectional area of the bellows, the known PVT properties of the confining mercury, and a correction function determined in a separate experiment in which the sample cell is filled with mercury alone. In the temperature range covered in these experiments (30–225°C), this apparatus is capable of measuring the specific volume of polymer samples at pressures to 2000 kg/cm² with an accuracy of 0.001–0.002 cm³/g.

Measurements on the three low-density polyethylene (LDPE) samples A, B, and C were performed along 17 isotherms for each sample and in pressure increments of 100 kg/cm², starting at $P = 100$ kg/cm². The results given for $P = 0$ are extrapolated. This procedure yields more reliable values for the specific volume at $P = 0$ because of some outgassing observed in most polymer melts.

Before testing, the samples were annealed at 100°C for 1 hr. The densities at 23°C after annealing were found to be 0.917 g/cm³ for samples A and C and 0.918 g/cm³ for sample B, in agreement with previous density data.¹

A problem with PVT measurements on polymers is their long duration (typically several hours in the melt). In the course of the measurements some degradation seems inevitable. We have no data on changes occurring in these samples during the measurements, but we tend to think that the degradation is not of such a magnitude as to affect the PVT data significantly. If degradation were a factor, we would expect the data on the three samples to show larger differences than those reported below, since the three samples show different thermal stabilities.¹

RESULTS AND DISCUSSION

The number of data points taken in this study is well over 1000. It would be impractical to reproduce them here. Instead, we present some of the data graphically and indicate mathematical fits to the data, which reproduce the measured specific volumes of the solid at zero pressure and of the melt at all pressures very accurately.

Figure 1 shows three selected isobars (0, 1000, and 2000 kg/cm²) in the PVT relationships of samples A, B, and C. These isobars were obtained by cross-plotting of the original (isothermal) data. It is at once obvious that the differences among the three samples are very minor, hardly more than the experimental uncertainty of $1-2 \times 10^{-3}$ cm³/g.

* We use pressure units of kg/cm² (kilogram-force per cm²). Other units may be obtained as follows: 1 kg/cm² = 9.80665×10^4 N/m² = 9.80665×10^4 Pa = 0.980665 bar = 0.967841 atm = 14.223 psi.

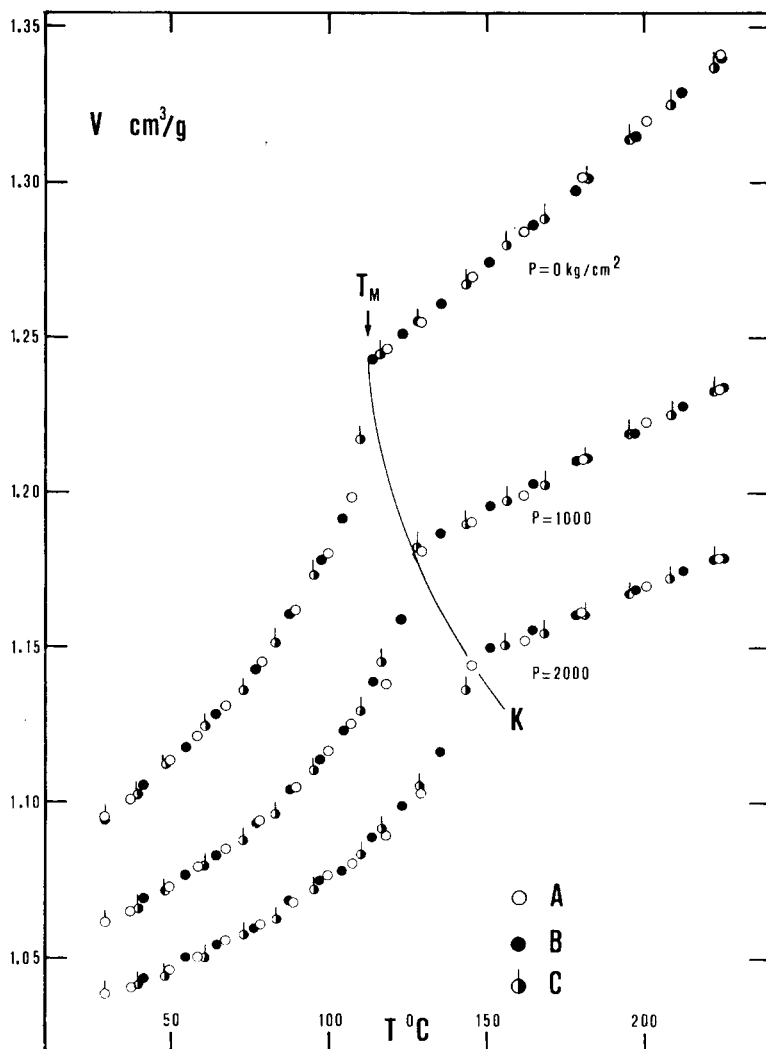


Fig. 1. Three isobars in the PVT relationships of low-density polyethylene samples A, B, and C. Line K marks the onset of crystallization on isothermal pressurization in these experiments: (O) A; (●) B; (◐) C.

Turning first to the zero-pressure isobar, we notice a well-defined end of the melting interval (T_M) at 111–112°C for all samples. This value of T_M is in complete agreement with thermo-optical determinations of T_M on the same samples done in our laboratory using a recording polarizing microscope in conjunction with a Mettler FP 52 hot stage. Line K gives the onset of crystallization on isothermal compression from the melt. The location of this line is noticeably dependent on the experimental time scale used. Line K *does not* represent the pressure dependence of the melting point, which would be observed in isobaric heating experiments.

The following equations can be fitted to the zero-pressure isobars:

$$T < T_M: \quad V(0, T) = A_0 + A_1 T + A_2 T^2 \quad (1)$$

$$T > T_M: \quad V(0, T) = V_0 \exp(\alpha_0 T) \quad (2)$$

The coefficients obtained by least-squares fitting of the data to these equations are listed in Table I. Each sample is considered by itself, but we also present the coefficients of a combined fit, in which all zero-pressure data of all three samples are considered together. The individual fits reproduce the measured data points to better than 0.001 cm³/g, whereas the combined fits lead to deviations as large as 0.003 cm³/g for some points.

In eq. (2), α_0 represents the isobaric volume expansion coefficient of the melt at zero pressure [$\alpha_0 = 1/V(\partial V/\partial T)_{P=0}$]. All three samples have an α_0 which lies within 2% of $6.8 \times 10^{-4} \text{C}^{-1}$, but sample A seems to have a slightly larger α_0 than the other two. Our values of α_0 may be compared with those found in other PVT work on polyethylenes. Olabisi and Simha³ have found $\alpha_0 = 7.80 \times 10^{-4}$ and $7.34 \times 10^{-4} \text{C}^{-1}$ for a sample of linear polyethylene (LPE, $\rho = 0.9794 \text{ g/cm}^3$) and branched polyethylene (BPE, $\rho = 0.9320 \text{ g/cm}^3$), respectively, while the zero-pressure data of Hellwege et al.⁴ lead to $\alpha_0 = 6.6 \times 10^{-4} \text{C}^{-1}$ for a low-density polyethylene (LDPE, $\rho = 0.9183 \text{ g/cm}^3$) very similar to ours. There thus seems to be a slight increase in α_0 with increasing linearity in polyethylenes. It is, however, very remarkable how close the specific volumes of very diverse polyethylenes in the melt really are (Fig. 2). In view of this plot, it is not very surprising that our three samples show practically identical zero-pressure isobars.

The pressure data are best discussed in terms of the so-called Tait equation. This equation describes the volume change along an isotherm in terms of two adjustable, temperature-dependent parameters $B(T)$ and $C(T)$ as follows:

TABLE I
Coefficients for the Fits to the Experimental Zero-Pressure Isobars, Eqs. (1) and (2)

Coefficient	Sample A	Sample B	Sample C	Combined
$A_0, \text{ cm}^3/\text{g}$	1.0885	1.0838	1.1038	1.0932
$A_1, \text{ cm}^3/\text{g } ^\circ\text{C}$	2.84×10^{-5}	1.68×10^{-4}	-5.85×10^{-4}	-1.71×10^{-4}
$A_2, \text{ cm}^3/\text{g } ^\circ\text{C}^2$	9.20×10^{-6}	8.34×10^{-6}	1.45×10^{-5}	1.10×10^{-5}
$V_0, \text{ cm}^3/\text{g}$	1.1484	1.1524	1.1516	1.1511
$\alpha_0, ^\circ\text{C}^{-1}$	6.95×10^{-4}	6.70×10^{-4}	6.73×10^{-4}	6.78×10^{-4}

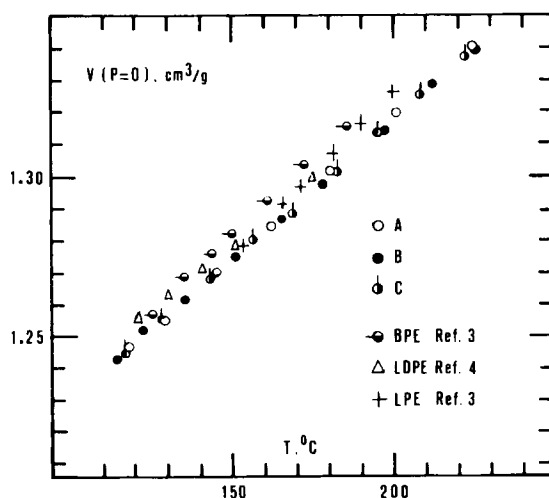


Fig. 2. Zero-pressure isobars of linear and branched polyethylene melts reported by different investigators: (O) A; (●) B; (◐) C; (◑) BPE, ref. 3; (Δ) LDPE, ref. 4; (+) LPE, ref. 3.

TABLE II
 Parameters Describing the Temperature Dependence of the Tait Parameter^a

Sample	B_0		$B_1, ^\circ\text{C}^{-1}$
	kg/cm ²	bar	
A	1968	1929	4.7005×10^{-3}
B	2005	1966	4.6005×10^{-3}
C	1904	1867	4.3914×10^{-3}

^a $B(T) = B_0 \exp(-B_1 T)$.

$$V(P, T) = V(0, T) \{1 - C(T) \ln [1 + P/B(T)]\} \quad (3)$$

It has been shown that this equation represents very accurately the compressibility behavior of a large number of liquids, including polymer melts, and also of glasses (see refs. 3 and 5–8). Normally a good fit to the data can be obtained using a “universal” value of $C = 0.0984$. The temperature dependence of B is usually found to be exponential:

$$B(T) = B_0 \exp(-B_1 T) \quad (4)$$

We find that the specific volume data of the polyethylene melts is well represented by the Tait equation with the universal value of C . Values of B_0 and B_1 obtained by least-squares fitting are listed in Table II. These coefficients, together with those of Table I, will reproduce all melt data to better than 0.001 cm³/g, with just a few points showing deviations as high as 0.002 cm³/g. The solid-state data, on the other hand, cannot be fitted to the Tait equation adequately: for the solid state, B is found to increase with pressure, in agreement with earlier observations.^{3,9,10} The equation of state of the melt in the form of eqs. (2), (3), and (4) lends itself to a calculation of the isothermal compressibility κ and of the isobaric expansion coefficient α as a function of temperature and pressure. The relevant equations are

$$\kappa(P, T) \equiv -1/V(\partial V/\partial P)_T = \{(P + B)[1/C - \ln(1 + P/B)]\}^{-1} \quad (5)$$

In particular, at $P = 0$;

$$\kappa(0, T) = C/B(T) \quad (5a)$$

and

$$\alpha(P, T) \equiv 1/V(\partial V/\partial T)_P = \alpha_0 + \kappa P(d \ln B/dT) = \alpha_0 - \kappa P B_1 \quad (6)$$

The zero-pressure compressibilities of the three samples calculated from eq. (5a) are again very similar. Over the whole experimental temperature range we find that sample A has the largest zero-pressure compressibility and sample B, the smallest; but the difference between A and B amounts to only 2.4% at 120°C, rising to 5.2% at 225°C, once again indicating the similarity of the PVT behavior of the three samples. The average value of $\kappa(0, T)$ of our samples is 5%–7% lower than that of the LDPE of Hellwege et al.^{3,4}

It might be added that an analysis of the melt data in terms of the Simha-Somcynsky hole theory of polymeric liquids¹¹ shows good agreement between theory and experiment, with reducing parameters very similar to those obtained for other branched polyethylenes.¹² The analysis has been presented elsewhere in a paper discussing the application of the Simha-Somcynsky hole theory to a series of different polyolefins.¹³

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